



# CHEMICAL ABSTRACTS

Vol. 17.

JULY 10, 1923

No. 13

## 1—APPARATUS

C. G. DERRICK

A simple device for the rapid preparation of fine asbestos fiber. B. L. JOHNSON. *Ind. Eng. Chem.* 15, 632(1923); illus. E. J. C.

The ardometer (pyrometer). D. FLIR. *Fuels & Furnaces* 1, No. 1, 17-20(1923).—The instrument is 5 in. high and 5 in. long weighing 1 lb. It consists of a telescope, between objective lens and the ocular lens of which is located a small thermoelement in a sealed glass tube. The hot junction of this thermoelement is soldered to a thin, blackened disk of Pt. The free ends of the couple are connected to a galvanometer which may be either indicating or recording. D. F. BROWN

The absorptiometer, an apparatus for the volumetric and gravimetric analysis of gases. L. MOSER. *Z. anorg. allgem. Chem.* 121, 313-8(1922).—An illustrated description of the *absorptiometer* previously described for the detn. of  $\text{PH}_3$  (cf. C. A. 16, 2822). The app. has since been tested with numerous gases and its manipulation simplified.  $\text{NH}_3$ , NO, HCl,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $(\text{CN})_2$ , HCN,  $\text{SiF}_4$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$ ,  $\text{O}_2$  and  $\text{Cl}_2$  can be accurately detd., but not  $\text{CO}_2$ . C. C. DAVIS

Plunger type of jelly-strength tester (a preliminary study). S. E. SHEPPARD AND S. S. SWERT. *Ind. Eng. Chem.* 15, 571-6(1923).—Exptl. results are given of tests made with a new balanced-beam plunger tester; the wt. is applied on the chainomatic principle. A satisfactory plunger is a frustrum of a cone, whose larger base presses on the jelly surface. The jelly mass must be sufficiently wide and deep to avoid spurious values. Jelly strengths can be detd. as accurately as viscosity, and expressed in absolute units as modulus of rigidity ( $N$ ), Young's modulus of stretch or compression ( $E$ ), or proof resilience per unit vol. ( $0.5 (f/E)$ , where  $f$  = load at elastic limit). Instrument makers and colloid chemists should agree upon a plunger type of instrument, with elimination of systematic errors. JEROME ALEXANDER

New apparatus of the Siemens-Zuckerwerke for testing oils. ANON. *Petroleum* Z. 19, 334-8(1923).—An app. for testing the dielec. strength of transformer and switch oils is described with illustrations. It consists essentially of two spark gaps, one of which is in the air and the other immersed in the oil to be tested. Movable indicators connected with the adjustment for lengthening the space of the gaps indicate on a gage the voltage attained when the limit of the oil has been reached. D. F. BROWN

A simple gas melting furnace. JULIUS MEYER AND HERBERT BRATKE. *Chem.-Ztg.* 47, 337(1923); 1 cut.—Cut a hole about 6.5 cm. diam. in the center of a strong asbestos board about 25 cm. sq. Knock the bottom out of a Hessian crucible of such size that when set in the hole it will extend through the board about 0.5 cm. Drill 3 holes about half way up the crucible and cement into them the stems of a clay triangle, forming a triangle to hold the porcelain or Hessian fusion crucible of about 50-g. capacity, about 8 cm. high. The cement is made by working 40 g. clay, 40 g. sand, 4 g. slaked lime, 2 g. borax and some chamotte powder into a tough dough with concd. water-glass soln. The Hessian crucible is then set in the hole in the board, the under side cemented to it, and after air-drying a few hrs. the union is carefully heated with a Meker burner. On top of the board, close to the crucible, cement 3 blocks of asbestos board to form feet 1.5-2.0 cm. high on which is placed an inverted, bottomless Hessian crucible about 12 cm. diam. and 12 cm. high, the hole in the upper end being covered with a sheet of asbestos with a hole in the center to admit a thermo-couple to the fusion crucible, which is also covered with an asbestos sheet. A sheet-Fe stack about 15 cm. diam. and at least 50 cm. high is put around the outer crucible and the whole placed on a tripod. With an empty crucible a fairly const. temp. of  $860^\circ$  can be reached in 10-15 min. with a Bunsen burner,  $1030^\circ$  with a Teclu burner, and  $1250$ - $1300^\circ$  with a Meker burner. J. H. MOORE

The Loring machine for adding liquids to powders. ANON. *Engineering* 115,

492-3(1923).—The app. is essentially a centrifugal machine in which the liquid is delivered inside the revolving basket, passes through a suitable screen and meets the falling powder in the outside compartment, in the form of a fine spray. The liquid is fed uniformly to the machine by passing through a soft rubber tube, which is intermittently rolled out. It falls on the apex of an indented cone, is thrown off by centrifugal force, passes through a thick felt liner inside the walls of the perforated basket and is very finely divided when entering the outer chamber. For accomplishing this purpose the basket is rotated about 2500 r. p. m. The powder is sifted round the basket by a revolving brush, passing over a wire grid made up of a wire coiled on the face of a perforated plate. Drawings are given to show the app., liquid feed and driving mechanism.

HOWARD E. BATSFORD

**Mercury-cleaning apparatus.** A. E. DIXON AND J. L. MCKEE. *J. Chem. Soc.* 123, 895-7(1923).—The Hg is contained in a cylindrical jar 30 cm. high and 5 cm. bore, the mouth of which is closed by a rubber stopper through which pass two tubes. One reaches just through the stopper and is attached to a suction pump. The other is a U-tube with its long arm through the stopper and its short arm drawn to a nozzle and bent outward somewhat. This arm is covered with a glass jacket which floats on the Hg. This covering tube has two narrow slots filed in it: one at the surface of the Hg and one 3 cm. above it. The U-tube has a small opening at the bottom, with a diam. about the same as the tube-bore (2.5 to 2.7 mm.). When the pump is started, the Hg is swept up the short arm of the U-tube and delivered in a fine spray of minute droplets, which strike against the wall of the glass jacket. Thence the comminuted Hg falls back into the mass of liquid, the circulation being continuous and complete. If the Hg is very foul the surface is covered with a layer of dil.  $\text{HNO}_3$  (1 : 20), not deep enough to flood the upper slot in the jacket.

H. JERMAIN CREIGHTON

**A post-office box for keeping analytical weights.** STEPHEN POPOFF. *J. Am. Chem. Soc.* 45, 1471(1923).

B. J. C.

**Laboratory table-top materials.** C. R. HOOVER. *Ind. Eng. Chem.* 15, 569-70 (1923).—Based on appearance, cost of installation and maintenance, thermal cond., combustibility, breakage of app. and resistance to  $\text{H}_2\text{O}$ , corrosive compds., non-aq. solvents, shock and abrasion, a refractory monolithic material like *Alberene* obtained the highest rating.

C. C. DAVIS

**Ozone generator with concentric electrodes.** R. GOEDICKE. U. S. 1,454,219, May 8.

**Sedimentation apparatus.** A. J. ARBUCKLE. U. S. 1,454,916, May 15. The app. is adapted for sedimentation of solids such as ore products which are withdrawn from a valved opening at the bottom of the app.

**Thermostat for ovens.** F. W. ROBERTSHAW AND G. A. ROBERTSHAW. U. S. 1,455,663, May 15.

**Apparatus for testing gases.** G. G. OBERFELL. U. S. 1,455,263, May 15. The app. is arranged to test flow and d. of gases and also to det. condensable vapor content (by use of activated charcoal).

**Portable apparatus for gas analysis.** F. A. MORELAND. U. S. 1,448,901, Mar. 20. The app. is generally similar to the Orsat type of app. Each of the chemical bottles is provided with a valved vent tube leading from its stopper to an expandable bag, which serves to prevent entrance of atm. O and thus assists in preventing deterioration of solns. in the bottles.

**Air or gas pyrometer.** I. LUNDGAARD. U. S. 1,455,633, May 15.

**Bag filtering apparatus for air or other gases.** S. J. MARX. U. S. 1,454,248, May 8.

**Device for indicating density or viscosity of liquids.** H. SPURRIER. U. S. 1,449,153, Mar. 20. Density of gases or density or viscosity of liquids is indicated by passing the fluid under test through a receptacle in which a const. vol. is maintained (for density indications) or a variant vol. is maintained (depending on the rate of overflow from an outlet) for viscosity tests of glazes or other liquid mixts. This receptacle is fed through a flexible tube and differences in the wt. of its contents change the level of the receptacle (which may be mounted on a spring) so that elec. contacts sound a signal bell whenever the receptacle and contents attain either a fixed max. or a fixed minimum wt.

**Filter for water or other liquids.** W. PATTERSON. U. S. 1,455,505, May 15.

**Filter for separating oil from water.** P. H. GENTZEL. U. S. 1,455,136, May 15.

**Electric water sterilizer and purifier.** W. T. HARRELL. U. S. 1,454,736, May 8.

**Automatic apparatus for controlling density of liquids.** J. L. MENNEL. U. S. 1,454,766, May 8. The density of liquids is controlled by a hydrometric balance which serves to actuate a pivoted launder through the medium of an elec. motor.

**Drying apparatus.** TEIJI MURATA. Japan. 41,191, Dec. 19, 1921. Within an endless band of wire gauze are placed elec. fans and nozzles for ejection of steam.

**Funnel stand.** NAGAO UENO. Japan. 41,193, Dec. 19, 1921. The stand is circular and rotates around the center.

**Rubber acid-proof containers.** J. E. PERRAULT. U. S. 1,454,687, May 8. Mechanical features.

**Column stills.** R. H. TWINING. U. S. 1,453,735, May 1. Diaphragm plates of column stills are provided with perforations through which rivet-shaped check valves extend to permit upward flow of vapor and check downward flow of liquid.

**Tunnel kiln.** G. W. BOOTH. Can. 230,803, May 8, 1923.

**Rabble stone for mechanical roasting furnace.** G. STÖHN. Can. 230,325, Apr. 10, 1923.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

**Prof. Dr. J. D. van der Waals, Sr.** P. ZEEMAN. *Physica* 3, 101-13(1923).—An obituary, with portrait. ANON. *Nature* 111, 609-11(1923). E. J. C.

**Unpublished chemical documents from the Goethe and Schiller archives in Weimar.**

JULIUS SCHIFF. *Chem.-Ztg.* 47, 385-6(1923). E. J. C.

**Bibliography, the foundation of scientific research.** WM. A. HAMOR. *Special Libraries* 1923, Mar.-Apr. no. E. J. C.

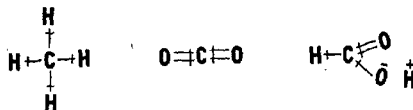
**A review of chemical investigations in the Dutch East Indies.** *Koninklijke Akad. Wetenschappen Amsterdam*, (separate) 1923, 26 pp. E. J. C.

**The progress of a research fellowship experiment.** W. E. TISDALE. *Ind. Eng. Chem.* 15, 641-2(1923).—About the Rockefeller Foundation fellowships. E. J. C.

**Symbols and formulas.** JAMES WALKER. *J. Chem. Soc.* 123, 939-46(1923).—Presidential address. From a historical review the author concludes that "a system of chemical formulation to have general currency must not be too elaborate."

AUSTIN M. PATTERSON

**Simplified method of writing "electronic" formulas.** R. J. WILLIAMS. *J. Am. Chem. Soc.* 45, 1272-3(1923).—The method uses a cross-line at the end of the bond to indicate the polarity of compds., *e. g.*,



H. JERMAIN CREIGHTON

**Atomic weight of titanium.** Preliminary paper. Analysis of titanium chloride. G. P. BAXTER AND G. J. FERTIG. *J. Am. Chem. Soc.* 45, 1228-33(1923).—The at. wt. of Ti has been detd. by means of analysis of  $\text{TiCl}_4$ . The rounded-off value 47.9 seems to be the most probable of those obtained.

H. JERMAIN CREIGHTON

**Atomic weight of gallium.** T. W. RICHARDS AND WM. M. CRAIG. *J. Am. Chem. Soc.* 45, 1155-67(1923).—The at. wt. of Ga has been detd. by means of analysis of  $\text{GaCl}_3$ , by essentially the same method employed in the case of  $\text{AlCl}_3$ . By taking the at. wt. of Ag as 107.88 and that of Cl as 35.458, the value 69.716 has been obtained for the at. wt. of Ga.

H. JERMAIN CREIGHTON

**The hypothesis of constant atomic radii.** R. W. G. WYCKOFF. *Proc. Nat. Acad. Sci.* 9, 33-8(1923).—From a collection of existing crystal-structure data it is concluded that these results are not in accord with an hypothesis of const. at. radii. These data, however, conform to the rule that in isomorphous crystals composed of only two kinds of atoms the interatomic distances have additive properties which can be illustrated through a summing up of "atomic radii." Among closely related substances variations from a rule of const. at. radii may be almost negligible; in other cases changes in interatomic distances may amount to several tenths of an Å.

RALPH W. G. WYCKOFF

**The absolute sizes of certain univalent and bivalent ions.** W. P. DAVEY. *Phys. Rev.* 19, 248-51(1922).—In continuation of the measurements of the radii of ions of alkali metals and halogens (cf. *C. A.* 16, 3777) the following values are given in Å. with the crystals used:  $\text{O}^{--}$  1.19 (CaO, BaO,  $\text{Cu}_2\text{O}$ ,  $\text{Ag}_2\text{O}$ ),  $\text{S}^{--}$  1.59 (CaS, ZnS, BaS),  $\text{Cu}^+$  0.76 (CuCl, CuBr), and 0.65 (CuI),  $\text{Ag}^+$  1.18 (AgCl, AgBr) and 0.85 (AgI),  $\text{Ti}^+$



1.77 (TiCl<sub>3</sub>), Mg<sup>++</sup> 0.90 (MgO), Ca<sup>++</sup> 1.25 (CaF<sub>2</sub>), Sr<sup>++</sup> 1.42 (SrO, SrF<sub>2</sub>), Ba<sup>++</sup> 1.56 (BaF<sub>2</sub>), Zn<sup>++</sup> 0.76 (ZnO), Cd<sup>++</sup> 1.11 (CdO), Cd<sup>++</sup> 0.95 (CdS), Ni<sup>++</sup> 0.88 (NiO), Sn<sup>++</sup> 0.93 (SnS), Pb<sup>++</sup> 1.33 (PbS). AgCl and AgBr are simple cubes of ions of side 2.76 and 2.89, resp. AgI is a diamond-cube of ions of side 6.53 (the shortest distance between centers of Ag and I is 2.83) (cf. C. A. 16, 3937). CuCl, CuBr and CuI are diamond-cubes of ions with sides 2.32, 2.49 and 2.63, resp. Ag<sub>2</sub>O and Cu<sub>2</sub>O consist of a body-centered cube of O<sup>--</sup> and a face-centered cube of the metal ion, and these 2 cubes interpenetrate like Cu<sub>2</sub>O (cf. W. H. and W. L. Bragg, *X-Rays and Crystal Structure*). The sides are 4.69 and 4.26, resp. The position of O<sup>--</sup> in Ag<sub>2</sub>O is in the center of a tetrahedron of Ag<sup>+</sup>, identical with I in AgI.

C. C. DAVIS

The universal distance of the order of  $10^{-8}$  cm. between the centers of the nearest atoms in solids. A. C. CREMORE. *Phys. Rev.* 19, 251-2(1922).—By using the at. model previously described (cf. C. A. 16, 377, 3583) it is found that 2 such atoms may unite to form a diatomic mol. Their distance is of the order of  $10^{-8}$  cm. and the common angle joining them and their rotation axes is approx.  $50^{\circ} 11'$ . Electrostatic forces alone can produce this stable equil. if the ratio of the major to the minor axes of the electrons is assumed to be approx. 3. To bridge a  $10^{-8}$  cm. distance requires 10,000-100,000 atoms and the smallest dimension of the mol. could be  $10^{-8}$ - $10^{-10}$  cm. Since  $10^{-8}$  cm. is the smallest actual dimension, this size must be attributed to the shape of the electron. Since electrons are universally present,  $10^{-8}$  cm. must be a universal order of distance.

C. C. DAVIS

Atomic projectiles and their properties. ERNEST RUTHERFORD. *Electrician* 90, 366(1923); cf. C. A. 17, 711.—An address.

C. G. F.

The importance in crystallography of the mathematical investigations of Schoenflies. PAUL NIGGLI. *Naturwissenschaften* 11, 277-82(1923).—The lasting importance of the work of Schoenflies (cf. *Krystallsysteme und Krystalstruktur* 1891) is discussed.

C. C. DAVIS

The crystal structure of the alums. R. W. G. WYCKOFF. *Am. J. Sci.* 5, 209-17 (1923).—Laue and spectrum photographic studies of K and NH<sub>4</sub> Al alums give  $T_h^6$  rather than the previously detd.  $T_h^4$  as their corresponding space group. The arrangement of the atoms within the unit cell is outlined, though no attempt is made to locate those atoms having variable parameters. The 12 water mols. fall into two groups of six each. It does not appear possible to arrange the NH<sub>4</sub> H atoms into a chemically plausible radical which will possess a symmetry in keeping with that of the rest of the crystal. The spectrographic observations show clearly the spurious character of some of the reflections upon which previous detns. of structure have been based.

RALPH W. G. WYCKOFF

Structure of the crystals of sodium bromate and sodium chlorate. N. H. KOLKMEIJER, J. M. BIJVOET AND A. KARSEN. *Z. Physik* 14, 291-5(1923).—The exptl. data from the powder photographic method of X-ray analysis are compared with those of Vegard (C. A. 17, 1356) and several of the parameter interpretations by the latter criticized. The structures and parameters found by K., B. and K. practically coincide with those of Dickinson and Goodhue (C. A. 16, 678).

G. L. CLARK

Crystal structure of basic beryllium acetate. W. H. BRAGG. *Nature* 111, 532 (1923).—The mol. of Be<sub>4</sub>O(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>6</sub> is a perfect tetrahedron. The crystal structure is that of diamond, a mol. replacing each atom of C. The C atom is itself tetrahedral, but is very nearly a sphere. The slight departure from sphericity is shown by the presence of a very small second order in the reflection by the tetrahedral plane of diamond. In the acetate this effect is large because of the much more pronounced tetrahedral character. The O atom must be at the center of the tetrahedron. The Be atoms lie on the lines from the center to the corners, and each (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) group must be associated in a very sym. manner with one of the tetrahedron edges.

G. L. C.

Röntgenographic determination of the structure of rolled metal foils. H. MARK AND K. WEISSENBERG. *Z. Physik* 14, 328-41(1923).—By means of geometric construction of schematic orientation spheres and reflection circles a simple explanation is arrived at for monochromatic X-ray patterns for statistically ordered cryst. media. For detg. the lattice orientation of the face-centered cubic metals Ag, Au, Cu, Pt and Al, a method is devised consisting in the direction of the X-ray beam ( $\lambda = 1.40$  and  $1.54 \text{ \AA.}$ ) parallel to the space diagonals. In rolled Ag foils there is a group of lattice orientations coexistent; parallel to the direction of rolling (about  $8^{\circ}$  deviation) is  $[11\bar{2}]$ ; parallel to the cross direction are  $[111]$  and such directions which lie in the  $(11\bar{2})$  plane and make an angle  $\leq 35^{\circ}$  with  $[111]$ ; parallel to foil normals lie  $[1\bar{1}0]$  and such directions which lie in the  $(11\bar{2})$  plane and make an angle  $\leq 35^{\circ}$  with  $[1\bar{1}0]$ . Besides

this group there is still another less prominent group of orientations. Cu, Pt, Al and Au foils all show the same lattice orientations: direction of rolling || [121]; cross direction || [111], foil normals || [110]. The glide planes are the rhombic-dodecahedral planes.

G. L. CLARK

**The crystal structure of iron-nickel alloys.** L. W. MCKEEHAN. *Phys. Rev.* 21, 402-7(1923).—Fourteen alloys were prepd. by melting together Armco Fe and electrolytic Ni, then swaging the castings and drawing and rolling into thin tapes. X-ray diffraction patterns were obtained from these after various heat treatments. With from 0 to 25% Ni the structure is chiefly body-centered cubic, with the parameter  $a$  increasing from 2.872 for pure Fe to  $2.89 \times 10^{-8}$  cm. With from 0 to 70% Fe, the structure is chiefly face-centered cubic, with  $a$  increasing from 3.510 for pure Ni to about  $3.60 \times 10^{-8}$  cm. Around 30% Ni either structure is on the verge of instability and both or either may exist. Cold working tends slightly to increase the parameter. The d's of pure Fe and Ni crystals are 7.775 and 8.953, resp. It is probable that Ni atoms differ from Fe atoms in possessing 6 electron orbits of a certain type instead of 4. The behavior of these atoms in forming crystals is consistent with the idea that the directions of closest approach in either pure metal are the normals to the planes of these orbits and that in the intermediate directions, 12 for Fe and 8 for Ni, the atoms cannot approach so closely due to protruberances on the atoms.

G. L. CLARK

**Crystal cleavage and crystal structure.** M. L. HUGGINS. *Am. J. Sci.* 5, 303-13 (1923).—A study of cleavage is illustrated by two-dimensional, unit-cube, and other diagrams of diamond, sphalerite, wurtzite, NaCl, pyrite, calcite, aragonite, graphite, Sb and Bi. The following rules are believed to govern crystal cleavage: (1) Cleavage tends to occur so as to leave the new surfaces electrically neutral. (2) Where some of the bonds in a crystal are weaker than others, cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones. (3) All bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area (of the cleavage plane). These rules furnish a valuable means of checking up proposed crystal structures. Their applicability to the compds. considered in this paper is evidence in favor of the structures assumed.

L. W. RIGGS

**Crystallographic study of  $\alpha,\gamma$ -diketohydrindene.** ANGELO PICHERRO. *Atti accad. Lincei* [v] 31, ii, 143-6(1922).— $\alpha,\gamma$ -Diketohydrindene, d. 1.37, forms crystals belonging to the bipyramidal tetragonal class of the tetragonal system,  $a : c = 1 : 0.9414$ .

J. C. S.

**Rhythmic crystallization.** HANS KÄGI. *Helvetica Chim. Acta* 6, 264-6(1923).—Menthyl  $\alpha$ -benzylacetoacetate is an excellent example of substances which show rhythmic crystn. The crystn. occurs at the rate of about one cm. per min. and can be followed in detail under the microscope. The racemic ester, m. 48-51°, may be crystd. in this form from a mixt. of alc. and glacial AcOH, or by the solidification of a supercooled melt of the ester. The *l*-ester, m. 68°, does not show rhythmic crystn. The evapn. of the solvent from a  $C_6H_6$  soln. of the racemic ester yields the best results. The rings vary in width from a fraction of a mm. to 5 mm., depending upon the amt. of ester per unit of surface, the rate of evapn. and the amt. of  $CaH_2$  remaining with the crystals. Several photographs of crystal formations are attached.

C. B. EDWARDS

**The relation between the linear growth of crystals and their initial size.** A. SHUBNIKOV. *Bull. acad. sci. Russ.* 1919, 1135-42.—Seven groups of six differently sized crystals of  $KAl(SO_4)_2$ , were equidistantly placed in circular crystallizers filled with solns. of the same substance satd. at different temps. If  $a$  is the wt. of a crystal before the expt. and  $b$  that after 8 days of undisturbed growth, the linear growth must be proportional to  $\sqrt{b} - \sqrt{a}$ . Comparing the latter value for each combination of 2 from 6 crystals of the same group, S. finds the min. probability of the larger crystals growing more rapidly = 0.67, with the av. probability = 0.78. The latter figure is larger the greater the initial difference in size of a pair thus compared.

M. S. KORSONSKY

**The size of the graphite molecule at high temperatures.** A. JOUNIAUX. *Bull. soc. chim.* 33, 260-7(1923).—C blacks formed by the thermal decompn. of org. compds. all contain graphite, the proportion of which in the mixt. increases with the temp. of formation. At about 3500° the system: amorphous carbon-graphite, is 100% graphite. When the mixt. formed at lower temps. is rapidly cooled to room temp. a false equil. is attained, the compn. corresponding nearly to that of the temp. of formation. This explains the variations in the results of different observers of the sp. heat of amorphous C and graphite at room temp. At higher temps. their results harmonize and approach agreement with the rule of Dulong and Petit. Applying the laws of dil. solns. to the data for the m. p. of solns. of C in Fe the mol. wt. of graphite proves to be 15.4. From the data for C in Co the mol. wt. is found to be 15.1. From these considerations it is

concluded that above about 1500° graphite is monatomic. This agrees with the value computed from the Dulong and Petit rule, taking the const. as 6.4 and the sp. heat of graphite at 1500° as 0.44.

**Density of magnesium from 20° to 700°.** J. D. EDWARDS AND C. S. TAYLOR. *Trans. Am. Inst. Mining Met. Eng.* 1923, No. 1242-N, 6 pp.—The d. of 99.99% pure Mg is as follows: 1.7388 at 20°; 1.560 and 1.565 at 667°; 1.562 at 673°. Values obtained above 700° were unreliable. The d. at the m. p. (about 650°) of the cryst. Mg is 1.642 and that of the liquid is 1.572; or the crystn. shrinkage is 4.2%. The rate of expansion of liquid Mg appears to be greater than that of the solid.

F. L. BROWNE  
BENJAMIN S. NEUBAUSSEN

**Determination of the vapor pressure of metallic arsenic.** SHINKICHI HORIBA. *Proc. Acad. Sci. Amsterdam* 25, 387-94(1923).—From the viewpoint of the theory of allotropy As is an interesting study. The results are given only for the gray modification. The method is that used by Smits and Bokhorst (*C. A.* 10, 2657) in studying P. The results agree closely with the equation  $T \log p = -7357 + 8.279 T$  (solid);  $T \log p = -2450 + 3.80 T$  (liquid),  $p$  being in atm. The triple point is between 817° and 818°, the corresponding pressure being 35.8 atm.

E. D. WILLIAMSON

**Behavior of ozone.** E. H. RIESENFELD. *Z. Elektrochem.* 29, 119-21(1923).—The following values have been detd. for some of the phys. const. of O<sub>3</sub>: m. p., -251.4°; b. p., -112.3°; crit. temp., -5°; crit. d., 0.537 and crit. pressure, 65 atm. Liquid O<sub>3</sub>, which is an intense deep blue-violet in color, is a normal liquid and contains no higher polymers of O. Conc'd. mixts. of O<sub>2</sub> and O<sub>3</sub> are very explosive, the quantity of heat set free being but slightly less than that evolved when H<sub>2</sub>-O<sub>2</sub> mixts. explode. The problem of the detn. of the O<sub>2</sub>-O<sub>3</sub> equil. is discussed.

H. JERMAIN CREIGHTON

**Triatomic hydrogen and the low-pressure localities.** JOSEPH LÉVINE. *Compt. rend.* 176, 705-6(1923); cf. Wendt and Landauer, *C. A.* 16, 1343.—In consequence of its lightness H constitutes at an altitude of 80 km., 2/3 of the atm. In places of reduced pressure, produced probably by the propagation of non-disruptive elec. discharges, the H is condensed to H<sub>2</sub> and the O<sub>2</sub> to O<sub>3</sub>.

L. W. RIGGS

**The relation between the hardness and atomic concentration of amorphous (isotropic) elements.** P. P. LAZAREV. *Bull. acad. sci. Russ.* 1918, 1259-60. The relations between the hardness and other physical properties of elements. *Ibid* 1918, 2241-5. The relation between the hardness and ultimate strength of elements. *Ibid* 1919, 1005-6.—If an atom upon the surface of a solid body is taken for the zero of coordinates, with the  $z$ -axis perpendicular to this surface, then for an elementary volume  $dv$  of the same body, located beyond the surface  $xy$ , but within the hemisphere of the zero atom's influence:  $dv = r^2 \cos \alpha d\alpha d\varphi dr$ , where  $r$  is the straight-line distance between the zero-atom and the elementary vol.,  $\alpha$  the angle between  $r$  and  $xy$ , and  $\varphi$  the angle between  $x$  and  $rz$ . The no. of atoms in the elementary vol. will be  $N dv f(r)$ , where  $f(r)$  is a pure function of distance, hypothetically equal for all elements. The vertical component of this force will be  $N dv f(r) \sin \alpha$ , and its integral for the whole hemisphere of influence of the radius  $R$ , will represent the force tending to preserve the relative position of the zero atom and

will give the measure of the hardness. So  $F_z = N \int_0^{\pi/2} \int_0^{2\pi} \int_0^R f(r) \times r^2 \times \cos \alpha \times \sin \alpha \times d\alpha \times d\varphi \times dr = N\pi \times \int_0^R r^2 \times f(r) \times dr = N\pi \times \theta(R)$ . According to the leading

hypothesis the expression  $\theta(R)$  is independent of the nature of the element; therefore  $F_z$ , or the hardness becomes proportional to  $N \times \text{const.}$ , a relation which was found to be empirically true for amorphous elements by Bottone, Turner and Benedicks. For the cryst. elements deviations are observed, which do not greatly affect the parallelism in graphs showing the periodical relationships: at. concn./at. weight and hardness/at. weight. The vibration no. for different atoms of solid elements must be proportional to  $\sqrt{H/A}$ , where  $H$  is the hardness (in its turn proportional to the quasi-elastic force of the solid element) and  $A$  the at. weight of the element. For the elements Pb, Ag, Zn, Cu, Al the following values are calcd.:

	$H \times 10^4$	$N \times 10^{-18}$	$N^2 \times 10^{-34}$	$(H/A) \times 10^4$
Pb	570	1.44	2.1	2.7
Ag	990	3.3	10.9	9.2
Zn	1100	3.6	13.6	16.9
Cu	1360	4.9	24.0	21.6
Al	820	6.0	36.0	30.4

The values of the last 2 columns coincide fairly well with the requirements of the theory, considering that  $H$  values are not quite definitely established and the cryst. form of the elements may also interfere. A certain constancy exists in the relationship of the hardness to the modulus of elasticity. For the same elements  $(H/E) \times 10^8$  averages 1.22 with a deviation of about 0.09. Pb makes an exception, but its elastic properties are the most difficult for exact detn. The same integral equation which gives the relationship between at. concn. and hardness may be applied to define the axial force, with which an atom situated somewhere within a solid elementary body is held in place by the aggregate of atoms located within its sphere of influence. The no. of atoms located along the cross-section, passing perpendicularly to the axis of tension, equals  $N^{1/2}$ , and the total internal force, acting parallel to the axis must be proportional to  $N^{3/4}$ . For the elements Ag, Au, Pt, Pd, Fe, roughly approx. agreement between the ultimate strength and at. wt.  $\times N^{3/4}$  is observed.

M. G. KORSUNSKY

**Kinetic interpretation of van't Hoff's rule.** C. E. GUYE. *Compt. rend.* 176, 835-8 (1923).—On the assumption that in order for the dissociation of a gas mol. to occur the velocity of collision must not be below a limiting value, calcs. are made showing the no. of such collisions per sec. in a mol. wt. of H at 0°. The time required for the dissociation of 1 cc. of H at various possible values of the limiting velocity is calcd. at 0° and at 10° and the ratio of these values is around 2, where the times are of ordinary length (not extending over years or not less than a sec.). It is pointed out that the same sort of calcn. for substances other than H would give similar values for the ratio. This is offered as a kinetic explanation of van't Hoff's rule that for a temp. rise of 10° the speed of a reaction is doubled.

JAMES M. BELL

**A new improvement of the equation of state for gases.** A. LEDUC. *Compt. rend.* 176, 830-3 (1923); cf. C. A. 16, 3579.

J. M. B.

**Test of van der Waals' equation as modified for the quasi-contraction of molecules, by means of the hydrogen isotherms of Kohnstamm and Walstra.** E. A. HOLM. *Arkiv. Mat. Astron. Fysik* 17, No. 20, 58 pp.; cf. C. A. 16, 3794.—From the data of K. and W.

(C. A. 8, 3263; 9, 747) the values of  $R$ ,  $a$  and  $b$  in the equation:  $p = (RT/v) \left[ 1 - (b/v) + \frac{3}{8} (b^2/v^2) - 0.0369 (b^3/v^3) \right] - (a/v^2)$  have been found for H. These are  $366.07 \times 10^{-6}$ ,  $43 \times 10^{-8}$ , and  $106 \times 10^{-8}$ , resp., whereas similar calcs. from Amagat's data yield the values:  $366.06 \times 10^{-6}$ ,  $31 \times 10^{-8}$ , and  $97 \times 10^{-8}$ .

JAMES M. BELL

**Relations of properties of liquids.** W. HERZ. *Z. Elektrochem.* 29, 110-1 (1923); cf. C. A. 16, 3797.—An equation has been deduced from Nernst's revised form of Trouton's law and the Clausius-Clapeyron formula, which gives a relation between the b. p. of a liquid and its vapor pressure at any temp. It is shown that at temps. which are neither too high nor too low the surface tension of non-associated liquids at the b. p. can be calcd. from the d. at the b. p., the b. p. and the mol. wt. of the liquid. For non-associated liquids the gas const. ( $R$ ) can be calcd. by means of the equation,  $Mp_s/Td_s = R/3.875$ , where  $M$  is the mol. wt. and  $p_s$ ,  $T_s$  and  $d_s$  are the crit. pressure, temp. and d. of the liquid.

H. JERMAIN CREIGHTON

**A theory of the viscosity of liquids.** C. V. RAMAN. *Nature* 111, 532-3 (1923).—In a liquid, momentum is transported partly, as in a gas, by the diffusion of mols. between parts of the medium, and partly, as in a solid, by transverse elastic waves, so that viscosity depends on their relative importance. Hence  $\eta_{\text{liquid}} = \eta_{\text{vapor}} e^{(E_2 - E_1)/RT}$ , where  $E_1$  is the work required to sep. a pair of mols. of the 1st (vapor) type and  $E_2$  those of the 2nd (solid) type. Since  $E_2 > E_1$ , the viscosity of the liquid will diminish with rising temp., just the opposite of the case of gases. But  $\eta_{\text{vapor}} \propto T^{1/2} e^{-E_2/RT}$  (Sutherland) where  $E_2 = E_2/6 = E_1$  (Chapman). Hence  $\eta_{\text{liquid}} = \eta_{\text{vapor}} e^{5E_2/RT}$ .  $E_2$  may be found from data for the viscosity of gases at different temps. and the viscosity of liquids may be immediately calcd. The formula holds for  $\text{C}_2\text{H}_6$  to within 0.2%.

G. L. CLARK

**The viscosity of liquid mixtures showing maxima.** D. B. MACLEOD. *Trans. Faraday Soc.* (preprint), 1923.—In a previous paper (C. A. 17, 1909) M. proposes an expression for the viscosity of pure liquids at different temps. which seeks to explain viscosity in terms of the free space within the liquid and of the mol. concerned. This expression has now been applied to liquid mixts., especially those showing maxima. The viscosity of liquid mixts. is a function of the constituents and of the mixt. The cause of the great increase of viscosity in mixts. showing maxima is the contraction which takes place on mixing; the change of d. being analogous to that produced on cooling a liquid. M. proposes the expression  $\eta = \eta_0 \{x/(x-c)\}^{A_1 + A_2 m}$

for the viscosity of liquid mixts., where  $x$  represents the free space of the mixt. per cc. of vol. before contraction;  $C$  the contraction per unit vol;  $A_1, A_2$  consts. for each constituent;  $v_1, v_2$  the percentage compn.; and  $\eta_0 = \eta_1 v_1 + \eta_2 v_2$ . Assuming  $x = 0.100$  cc. for such mixts. as pyridine and water,  $\alpha$ -picoline and water, and 2,6-lutidine and alc., M. obtains values for the viscosity which agree very well with the exptl. values. Curves are given for several mixts. showing the variation of viscosity with compn.

L. M. HENDERSON

A new explanation of diffusion. ALEXANDR BAYK. *Chem. Listy* [9] 16, 295-9.—Fick's theory for the diffusion of liquids (*Ann. Phys. Chem.* [ii] 94, 59(1856)), is discussed, and its exptl. basis questioned. Certain discrepancies between the results calcd. on this theory and those obtained experimentally by Voit (*Ann. Phys. Chem.* [ii] 130(1867)), are pointed out. The technic of optical methods for the detn. of rates of diffusion is examd., and possible sources of error are suggested. Weber's confirmation (*Ann. Phys. Chem.* [iii] 7, 469, 536(1870)) of the applicability of Fourier's law to the diffusion of liquids is shown to be doubtful, and the necessity for a reconsideration of the whole question emphasized. The mechanism of the diffusion of liquids is then discussed from first principles, and the use of the conception of limiting states of solns. in helping to elucidate the problems of diffusion of liquids is substantiated.

J. C. S.

The Tyndall phenomenon in liquids. RICHARD GANS. *Physik. Z.* 24, 65-6 (1923).—The  $H_2O$  for the expts. was passed through a colloidion ultrafilter to free it from suspended matter. When illuminated by a beam of sunlight from a heliostat and observed at right angles to the beam it showed a slight Tyndall effect. An 18% cane-sugar soln. showed a much stronger effect. The scattered light proved to be completely polarized, indicating that the dissolved mols. are spherical in shape. F. L. BROWN

Cohesion and adhesion. WILSON TAYLOR. *Phys. Rev.* 19, 413-4(1922).—Measurements were made of the surface tension of Hg spheres 0.006-1.5 mm. in diam. suspended freely from the lowest rims of  $H_2O$  drops. The vertical lift on the Hg by the surface tension of  $H_2O$  was always greater than the wt. of Hg except where the spheres, because of size, were about to fall. At this point these 2 forces were equal. For the smallest sphere, the lift was 7 times the wt. With Hg spheres 0.002-2.25 mm. in diam. suspended from a glass surface, the lift, as the spheres increased in size, decreased from approx. 13,000 to 2.29 times the wt. Calcd. on the surface tension of glass (239 dynes per cm.) this ratio decreased from 6,000 to 1. The same law was found for solid bodies suspended from  $H_2O$  and small solids adhering to each other with a liquid medium. Cohesion and adhesion are surface-tension forces which exist about all free masses, mol. or larger, attaching themselves to each other in the periphery of the contact area and binding the 2 masses together in 1 enveloping surface-tension force. There is no evidence of any mol. attraction between the 2 masses in the contact area itself, but an actual pressure of the 1 mass on the other, reaching in the  $H_2O$  mol. approx. 11,000 atm.

C. C. DAVIS

Interfacial tension. J. R. POUND. *J. Chem. Soc.* 123, 578-99(1923).—The interfacial tensions of pure liquids in contact with water are const. at 1 temp. The present values are in general agreement with previous detns. The interfacial tension between 2 liquids is the less the greater their mutual soly. The interfacial tensions of com. liquids or oils in contact with water usually vary with the age of the interface; they nearly always decrease with time. In these cases the interfacial tensions are less than the difference of the surface tensions of the satd. liquids. The diminution of interfacial tension with time is pronounced even when chem. action between the liquids is improbable, e. g., with paraffin oils and water. It may be concluded that a mixt. (of oils) will always give a variable interfacial tension with water owing to phys. concn. at the interface of the components giving the lowest interfacial tension. Further, when chem. change occurs at the interface, the tension will alter; in particular the fatty oils suffer hydrolysis in contact with water, and the resulting changes at the interface help in the lowering of the interfacial tension. The rate of lowering of interfacial tension frequently becomes slower as the interface ages; however, it can scarcely be said that there is any inferior limit to interfacial tension but zero.

JAMES M. BELL

Note on azeotropic mixtures. SYDNEY YOUNG. *Proc. Roy. Irish Acad.* 36, Sec. B, No. 3, 22-30(1922).—The probability that 2 or 3 given liquids will form a binary or ternary azeotropic mixt. (mixt. of const. b. p.) may be detd. in a few cases. Two factors enter into this problem: the deviation of the liquids from the normal and the difference between the b. ps. of the liquids. Where the latter is small, a small deviation of the liquids from the normal will give a b. p. curve with a max. or minimum in it, but where the difference in the b. ps. of the liquids is greater, a greater deviation of the liquids from normal is necessary for a max. or minimum to appear in the b. p. curve.

Binary and ternary mixts. of water, lower alcs. of the EtOH series, hexane, benzene, toluene are discussed.

**Colloid chemistry.** W. D. BANCROFT. *J. Am. Inst. Elec. Eng.* **42**, 367-71(1923).—A popular presentation of numerous applications of colloid chemistry. M. KNOBEL.

**The rigidity of jellies.** F. MICHAUD. *Ann. phys.* **19**, 63-80(1923).—For the methods employed see C. A. **16**, 3242. When a pressure  $P$  is applied to one end of a cylinder of gelose or gelatin jelly, the displacement along the axis increases linearly with  $P$ , then falls off slightly. On releasing  $P$  the residual deformation is less than 10% of the total and soon falls to 0. If the elastic limit is passed, there is a dislocation indicated by the appearance of heterogeneity, portions becoming liquid and flowing in among the remaining solid parts. The original jelly can be restored only by melting again and allowing it to set. The "apparent liquids" are classified as (1) true liquids, which are homogeneous condensed fluids in which Brownian movement is discernable; (2) jellies, which are homogeneous media differing from elastic solids only in degree of rigidity; (3) the non-homogeneous media obtained when jellies are agitated while cooling so that they contain jelly parts floating in liquid. These systems have no definite phys. consts. For jellies extrapolation of the curve of rigidity vs. concn. indicates that the rigidity becomes 0 before the concn. This indicates that pure  $H_2O$  has zero rigidity, in disagreement with the conclusions of Schwedoff. For the influence of acids, bases, salts, and org. compds. on the rigidity of gelose and gelatin jellies see C. A. **17**, 1360.

F. L. BROWNE

**Evidences of a structure in gelatin gels.** R. A. GORTNER AND W. F. HOFFMAN. *Proc. Soc. Exptl. Biol. Med.* **19**, 252-3, 257-64(1922).—Gelatin gels of different concns., when dried, will again imbibe  $H_2O$  according to their original  $H_2O$  content and independently of the amt. of surface exposed. A 10% gel dried to less than 3%  $H_2O$  content had imbibed at the end of 72 hrs. 6.45 g. of  $H_2O$  per g. dry gelatin, as contrasted with 4.3 g.  $H_2O$  for a 40% gel similarly treated. Gelatin gels have a structure fixed at the time of gelation, and not appreciably altered by drying at room temp. A crystal structure in which the gelation temp. is actually the m. p. of the crystals would explain the phenomena.

C. V. B.

**Smokes. II. A method of determining the size of the particles in smokes.** R. WHYTLAW-GRAY AND J. B. SPEAKMAN. *Proc. Roy. Soc. (London)* **102A**, 615-27(1923); cf. C. A. **17**, 1910.—The mass dispersed in a given vol. is detd. by weighing the particles, after collection upon a combined filter and precipitator. When these data are combined with the number per cc., as found previously, the size of the particles is obtained. The wt. of dispersed material per l. and the av. wt. of the particles, resp., are shown as a function of the time, in 2 curves. There is a max. at about 0.5 hr. in the first curve. This is explained by amicros going through the filter. Evidence for this was obtained which indicated that during the early history of an aerosol a large proportion of the mass is dispersed in the mol. state or as amicroscopic particles. The slope of the later sections of this curve gives a measure of the loss by settling. The degree of complexity of the aerosol, as a function of the time, was detd. by examn. of the particles deposited upon a glass plate. This complexity, when multiplied by the corresponding number of particles per cc. (corrected for the loss by settling), gives a fairly const. value, showing that the growth of the particles is due solely to aggregation.

H. C. PARKER

**Physicochemical study of nitrocellulose in organic media. I and II.** I. NEWTON KUGELMASS. *Rec. trav. chim.* **41**, 751-63(1922).—The exptl. study of the mechanism of the entrance into soln. in mixts. of solvents leads to interesting observations on the manner in which nitrocelluloses behave at low temps. If nitrocellulose is placed in contact with dry  $Et_2O$  at low temps. suspensoids with a blue opalescence are formed above the sharply sepd. nitrocellulose mass. In abs. EtOH a series of distinctly sepd. layers is observed: the upper layer is a soln. free from the Tyndall effect and slightly more viscous than EtOH itself; under it lies a turbid layer of swollen nitrocellulose in EtOH; the lower layer contains fibrous flocks and in the bottom lies the unchanged nitrocellulose. Given that nitrocellulose is insol. in EtOH and in  $Et_2O$  at ordinary temps. but sol. in mixts. of them, the above phenomena were studied quant. The residue from the  $Et_2O$  soln. contained 13.75% N unless it was centrifuged at 10,000 r. p. m., after which it was no longer opalescent but showed the Tyndall effect. The residue now contained 11.20% N, i. e., cellulose dinitrate (11.13% N). The residue from the EtOH soln. contained 14.02% N, i. e., cellulose trinitrate (14.17% N). A modified method for prep. nitrocelluloses is also described. This sep. soly. only occurs at low temps. K., therefore, investigated the formation of the  $Et_2O$  sol to see if the general principles of colloidal chemistry hold. The change in viscosity of nitrocellulose

sol in  $\text{Et}_2\text{O}$  with the temp. was detd. in a Scarpa viscosity app. from room temp. to  $-100^\circ$ . There is a crit. temp. at  $-20^\circ$ , when nitrocellulose begins to dissolve, and on lowering the temp. to  $-98^\circ$  the viscosity approaches an asymptotic limit value. The Tyndall effect also begins to appear at  $-20^\circ$  and seems to increase at about the same rate as the viscosity. Quant. studies on the peptization, coalescence, protective power and crit. temp. of coalescence as criteria of colloidal stability, etc., for the nitrocellulose sol in  $\text{Et}_2\text{O}$  show that the laws of colloidal chemistry of aq. systems hold similarly in a nonaq. colloidal system. Some theoretical considerations are developed on the mechanism of the formation of a nitrocellulose sol in  $\text{Et}_2\text{O}$ . E. J. WITZMANN

**Classification of dispersed systems compared with the mechanism of "true" and "colloidal" solvation and precipitation.** P. P. VON VEIMARN. *Kolloid-Chem. Beihefte* 17, 72-114(1923); cf. C. A. 16, 161.—Wo. Ostwald's classification of dispersed systems may be augmented by also considering the degree of dispersion. Thus by further including as dispersions the particles  $> 0.1\mu$ , as dispersoids those between  $0.1\mu$  and  $1\mu$  and as disperses those of  $1\mu$  and smaller, instead of 9, there are obtained 27 degrees of dispersion. This is a classification, therefore, not only according to phasal variations but also according to the degree of subdivision of the dispersed phase. A. MUTSCHILLER

**An increase in density in thin films.** ELIZABETH R. LAIRD. *Phys. Rev.* 19, 384-5(1922).—By interferometer detns. the wt. of celluloid films was not proportional to thickness. The values of  $n$  for varying thickness, the displacement of fringes, the area of films and their wt. were detd. No change in  $n$  occurred with decreasing thickness, the value being 1.50-1.51. The  $d$ . down to a thickness of  $400\mu$  remained approx. 1.41 g. per cc. but then increased to approx. 2 at  $60\mu$  and to approx. 2.5 at  $30\mu$ . C. C. DAVIS

**Relation of hydrogen-ion concentration to flocculation of a colloidal clay.** R. BRADFELD. *J. Am. Chem. Soc.* 45, 1243-50(1923).—Colloidal clay is flocculated by  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{HOAc}$  at about the same  $p_{\text{H}}$  value (3.5), but a slightly greater acidity is required with citric acid. Change in the  $p_{\text{H}}$  value from 6.2 to 8 increases the electrolyte requirement ten-fold, in mixts. of  $\text{KCl}$  and  $\text{KOH}$ . Similar variations in the flocculating power with change in the  $\text{H}$ -ion concn. are exhibited by  $\text{K}_2\text{HPO}_4$ , but the electrolyte requirement is higher. The results of the investigation indicate that the flocculating power of K salts is influenced by the nature of the anion even compared at the same  $p_{\text{H}}$  values. H. JERMAIN CREIGHTON

**Colloidal membrane for liquid junctions.** H. FALES AND M. J. STAMMOLMAN. *J. Am. Chem. Soc.* 45, 1271-2(1923).—By the use of a colloidal membrane at liquid junctions mech. intermixing of one liquid into another can be prevented in the measurement of  $\text{H}$ -ion concns. by the e. m. f. method. This type of junction is only applicable to those solns. whose ions the membrane is equally permeable. H. J. C.

**Adsorption. IV. Charge reversal of some colloids.** N. R. DHAR AND K. C. SEN. *J. Phys. Chem.* 27, 376-83(1923).—Freshly pptd.  $\text{Fe}(\text{OH})_3$  passes into a negatively charged colloid when shaken with  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{H}_2\text{C}_4\text{H}_7\text{O}_6$ ,  $\text{H}_2\text{MoO}_4$ , or meconic acid. When the hydroxides of  $\text{Cu}$ ,  $\text{Al}$ ,  $\text{Cr}$ ,  $\text{Zn}$  and  $\text{Co}$  are peptized by caustic alkalis, they are negatively charged because of the adsorption of  $\text{OH}$  ions. The ammoniacal solns. of the hydroxides of  $\text{Cu}$ ,  $\text{Cd}$ ,  $\text{Zn}$  and  $\text{Ni}$  contain negatively charged hydroxides of the respective metals. Positively charged  $\text{As}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_3$  sols may be obtained by the adsorption of suitable ions, as  $\text{Th}^{++}$ ,  $\text{UO}_2^{++}$ ,  $\text{Al}^{+++}$ ,  $\text{Ba}^{++}$  and  $\text{H}^+$ . Gelatin, as a protective colloid, is used in some of these cases. The blue color of ammoniacal cupric salt solns., in Fehling's soln., in solns. of  $\text{Cu}(\text{OH})_2$ , in caustic alkali, in the mixt. contg. alkali, cupric salts and  $\text{C}_6\text{H}_5(\text{OH})_2$  or sugars is most likely due to peptized negatively charged  $\text{Cu}(\text{OH})_2$ .  $\text{Fe}(\text{OH})_3$  is a good adsorbent for ferric salts. Ions of higher valency are not adsorbed more strongly than those of lower valency. F. E. BROWN

**Studies in ionic adsorption.** N. G. CHATTERJEE. *J. Proc. Asiatic Soc. Bengal Proc. 8th Indian Sci. Cong.* 17, cxxx(1921).—The action of chemically pure hydrated  $\text{MnO}_2$  as an adsorbent has been observed in the case of a large no. of electrolytes. The following results have been obtained: The cation is much more adsorbed than the anion. The process of adsorption is very quick and the temp. coeff. is extremely small. Relatively more is adsorbed from a dil. soln. than from a concd. one. Nonelectrolytes that decrease the surface tension increase adsorption. The at. proportion of the bivalent ions adsorbed is the same for those electrolytes which have the same degree of ionization at the same dilution. Freundlich's simple law of adsorption is more or less obeyed. E. J. C.

**The adsorption of carbon monoxide and hydrogen by platinized asbestos.** F. H. POLLARD. *J. Phys. Chem.* 27, 356-75(1923).—The adsorption of  $\text{H}_2$ , of  $\text{CO}$ , of  $\text{H}_2$  in  $\text{N}_2$ , of  $\text{CO}$  in  $\text{N}_2$  and of a mixt. of  $\text{CO}$  and  $\text{H}_2$  by  $\text{Pt}$  was detd.  $\text{Pt}$ -black formed

Pt-sponge when heated above  $100^{\circ}$  in freeing it from the gas of one expt. in prepn. for the next. This caused a marked decrease in adsorptive power. For nearly all of these expts. com. platinized asbestos was used. The app. consisted of an adsorption bulb connected to a small drying bulb. This bulb was connected to a manometer and to a gas buret which also served as the bulb of a Toepler pump for evacuating the system. For a part of the expts. the stopcocks were lubricated with  $P_2O_5$  but delay in reaching equil., leakage, and setting led to trying a vaseline-rubber lubricant. This poisoned the Pt. Even placing a U-tube filled with glass wool and immersed in liquid air between the Pt and the stopcocks did not entirely prevent the poisoning of the Pt. Then,  $N_2$  was introduced with the  $H_2$  or CO in quantities sufficient to equal the atm. pressure so that  $P_2O_5$  could be used as a lubricant for the stopcocks. Seven tables of data including more than 100 observations are given. The highest adsorption of  $H_2$  by Pt-black was 369.9 vols. After heating at  $250^{\circ}$  Pt-black prepd. in the same way, absorbed only 84.8 vols. As the pressure varied from 5.5 mm. to 402.8 mm. the vols. of CO adsorbed at  $0^{\circ}$  varied from 33.1 to 96.3. As pressures varied from 9.0 mm. to 130.0 mm. the vols. of  $H_2$  adsorbed varied from 25.0 to 152.5. At atm. pressures 200 vols. of  $H_2$  and 300 vols. of CO were adsorbed by platinized asbestos. The adsorbed gas could be completely removed but the adsorption curve did not coincide with the removal curve. No evidence was found to support the contention that a compd. forms in the case of either  $H_2$  or CO adsorbed by Pt. If CO is introduced into the adsorption chamber after equil. between platinized asbestos and  $H_2$  is reached, the CO displaces the hydrogen already adsorbed. This accounts for the poisoning effect of CO on Pt used as a catalyst in hydrogenation.

F. E. BROWN

The nature of charcoal "sorption." H. H. SHELTON. *Phys. Rev.* 19, 253(1922).—According to McBain (cf. C. A. 4, 706; 13, 220) "sorption" is composed of adsorption on the surface and absorption (*i. e.*, solid soln.) into the interior. By plotting pressure-time curves for gases and concn.-time curves for solns., 2 distinct sections of the curves are sepd. by a bend. This indicates a dual action, the second beginning only after the first is nearly complete. Since soln. should begin as soon as adsorption, the bend is not accounted for. It is suggested that the second section of the curve is due to diffusion into the more inaccessible channels which cannot be expected to take place to any extent until the easily accessible or directly exposed portions are satd. C. C. DAVIS

Adsorption by activated sugar charcoal. II. F. E. BARTELL AND E. J. MILLER. *J. Am. Chem. Soc.* 45, 1108-15(1923); cf. C. A. 16, 3784.—Data are presented in support of a theory of hydrolytic adsorption of electrolytes from soln. by activated, ash-free charcoal. The adsorption of dyes is accompanied by marked hydrolysis and liberation of alkali which remains in soln. Pure charcoal does not adsorb the strong inorg. bases. The adsorption of a salt of a strong base and a readily adsorbed acid results in the liberation of the base. The introduction of the OH or  $NH_2$  group decreases the adsorption of the acid into which it is introduced, the effect of the latter group being considerably greater than that of the former.

H. JERMAIN CREIGHTON

The combination between organic dyes and inorganic substrates. H. RHEINBOLDT AND E. WEDERKIND. *Kolloid-Chem. Beihefte* 17, 115-88(1923).—An extensive review reveals the fact that in general the basic substrates form stable compds. with acid dyes and acid substrates with basic dyes. Exceptions are due to faulty technic and the use of impure or poorly defined substrates or dyes. Only a washable complex is considered as an adsorption compd. A large no. of substrates examd. can, with the exception of amorphous C, be grouped as those which adsorb acid and those which adsorb basic dyes of either mol. or colloid dispersion. Prepn. the substrates by different methods and varying the conditions furnishes evidence that the charges of substrates are not due to adsorbed ions but that they reside in their surface as unoccupied cohesive valences in agreement with Perrins' rule for contact electrification. The term *adsorption electroaffinity* or "*electroaffine*" adsorption are introduced. Expts. with carefully dialyzed 0.02% solns. of a large no. of dyes (except naphthol yellow as 0.1% soln.) and substrates which are washably dyed by basic dyes are not dyed by acid dyes and *vice versa*. This rule holds for the various oxides ( $SiO_2$ ,  $TiO_2$ ,  $SnO_2$ ,  $ZrO_2$ ,  $ThO_2$ ,  $CeO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$ ,  $Cr_2O_3$ ,  $BeO$ ,  $ZnO$ ,  $MgO$ ,  $PbO$ ) and for the sulfides ( $As_2S_3$ ,  $Sb_2S_3$ ,  $CdS$ ) and chloride ( $AgCl$ ). Only in case of amorphous C were both kinds of dyes adsorbed. "Electroaffine" adsorption is therefore caused by the free cohesion valences at the surface of the substrate, which are neutralized by a monomol. layer of the oppositely charged dye.

A. MUTSCHELLER

Certain physical properties of arsenic trioxide in water solution. E. ANDERSSON AND L. G. SRÖRY. *J. Am. Chem. Soc.* 45, 1102-5(1923).—Accurate data are given for the *d*, *n*, soly., H-ion concn. and mol. wt. of  $As_2O_3$  in aq. soln. H. J. CREIGHTON



**Mutual solubility of liquids. I. Mutual solubility of ethyl ether and water.**  
**II. Solubility of water in benzene.** A. E. HILL. *J. Am. Chem. Soc.* 45, 1143-55 (1923).—It is proposed that all methods for detg. soly. be classified on the basis of the phase rule, as *thermostatic*, *plethostatic* or *barostatic*. A thermostatic method is described for the detn. of the mutual soly. of liquids. The mutual soly. of Et<sub>2</sub>O and H<sub>2</sub>O has been detd. between -3.83 and 30° by this method. The soly. of H<sub>2</sub>O in C<sub>6</sub>H<sub>6</sub> has been detd. by means of AgClO<sub>4</sub> between 5.4 and 69.5°.

H. JERMAIN CREIGHTON

**Solubilities of certain metallic chlorides in selenium oxychloride.** C. R. WISE. *J. Am. Chem. Soc.* 45, 1233-7 (1923).—The solubilities of 22 metallic chlorides in SeOCl<sub>2</sub> have been detd. at 25°. The results show that while a no. of the chlorides do not unite with SeOCl<sub>2</sub>, others form characteristic double compds., e. g., KCl<sub>2</sub>SeOCl<sub>2</sub>.

H. JERMAIN CREIGHTON

**Solubility of mannitol in mixtures of ethyl alcohol and water.** H. J. M. CREIGHTON AND D. S. KLAUDER, JR. *J. Franklin Inst.* 195, 687-91 (1923).—"The soly. of mannitol in alc.-H<sub>2</sub>O mixts., contg. 0, 20, 40, 60, 80, and 100% EtOH, has been detd. at 0, 15, 25, 35, 50 and 60°. Within the temp. range studied, the log of the soly. of mannitol in mixts. of EtOH and H<sub>2</sub>O at any temp. is a function of the soly. in pure H<sub>2</sub>O, the mol. fraction of alc. present in the solvent and the abs. temp.; while at a particular temp., it is a function of the solubilities in the pure components and the mol. fractions of these components."

JOSEPH S. HEPBURN

**Investigations on the theory of solutions.** P. P. LAZAREV. *Bull. acad. sci. Russ.* 1918, 207-14.—An elementary vol.  $d\sigma$  of a soln., identified by the concn.  $N_1$  of the solvent and  $N_2$  of the solute, is located within the hemisphere of intermol. action of the radius  $R$ , at the distance  $r$  from some surfacial mol. of the solid interstitial substance, having the mol. concn.  $N$ . Making this surfacial mol. the zero of coordinates, and the surface of the solid substance the plane  $x-y$ , this elementary vol. of the soln.  $d\sigma$  becomes identified in space by the distance  $r$ , the angle  $\theta$  between plane  $x-r$  and axis  $x$  and the angle  $\alpha$  between the plane  $x-y$  and  $r$ . The elementary forces acting between the zero point mol. of the solid and the mols. of the solvent and the solute, resp., must be proportional to the no. of mols. in the elementary vol. and also to some unknown function  $\phi_1(r)$  and  $\phi_2(r)$  of distance, and to some const.  $k_1$  and  $k_2$  characteristic for the interacting mols. Therefore  $dF$  (elementary force) =  $[k_1\phi_1(r)N_1 + k_2(r)N_2] \times r^2 \times \cos\alpha \times d\theta \times dr$ . The triple integral of this expression, taken for the whole hemisphere, and having the final form  $\pi[N_1F_1(R) + N_2F_2(R)]$ , where  $F_1$  and  $F_2$  stand for the unknown functions of distance for both kinds of mols., represents the force of attraction solution-solid acting parallel to the axis  $z$ . Subtracting from it the force developed within the solid which tends to keep the zero-point mol. in place, and whose expression will be:  $F = \pi NF(R)$ , L. obtains for the force of dissoln. the expression:  $F = \pi[N_1F_1(R) + N_2F_2(R) - NF(R)]$ . As the values of  $F(R)$ ,  $F_1(R)$  and  $F_2(R)$  remain const., provided the solid and the soln. have a thickness far in excess of  $R$ , the whole expression for the force  $F$  can be reduced to  $F = \beta_1N_1 + \beta_2N_2 - \beta N$ . This shows, that (1) solid substances of a high  $N$ , and consequently of a great hardness must display lower forces of dissoln.; (2) satd. solns. are obtained when  $\beta_1N_1 + \beta_2N_2 = \beta N = \text{const.} = C$ . Replacing  $\beta_1$  and  $\beta_2$  by  $(a_1/D) + b_1$  and  $(a_2/D) + b_2$ , where  $a/D$  stands for the electrostatic and  $b$  for electrodynamic intermol. relations, and assuming the contraction in dissoln. to be negligible, L. obtains the equation:  $N_s$  (the max. concn. of the solute) =  $[D^3C - D(a_1 + b_1D)N_0]/[a_2 - a_1 + D(b_2 - b_1)]$ , where  $N_0$  is the total concn. of the soln. at the beginning of dissoln. Walden's rule:  $N_2 = AD^3$  can be regarded as a special case valid for certain relations between the  $a$ 's and  $b$ 's.

M. KORSUNSKY

**Solubility relations in mixtures containing polar components.** F. S. MORTIMER. *J. Am. Chem. Soc.* 45, 633-41 (1923).—The deviations from Raoult's ideal soly. law are proportional to the magnitude of the differences of the internal pressures of the components of the system. The Raoult expression is  $\log N = -(Lf/4.58)(1/T - 1/T_m)$ , where  $N$  is the mol. fraction of the solute at  $T$ ,  $T_m$  the m. p. of the solute,  $L$  the mol. latent heat of fusion and  $f$  a factor relating to internal pressures of solute and solvent. In plotting  $\log N$  against  $1/T$ , the slope of the straight line is  $Lf/4.58$ , the ideal slope. The quantity  $f$  can, therefore, be found from the ratio between the experimentally found slope for the values  $\log N$ ,  $1/T$  and the ideal slope. The relative internal pressures of 15 liquids so calcd. are in excellent agreement with the relative values by other methods. With naphthalene as the standard, a table of relative internal pressures is given for 70 substances. The values in the table can be employed in calcg.  $f$  for any pair of the substances.

JAMES M. BELL

The chemico-physical foundation of evaporation and of the solution in mother

liquors. O. KRULL. *Kali* 16, 377-81, 393-7, 413-8, 432-7, 449-55(1922).—This study was made on various mixts. of solns. of KCl, MgCl<sub>2</sub>, MgSO<sub>4</sub> and NaCl, the results being illustrated by 11 three-component and 5 two-component diagrams.

L. W. RIGGS

**Anomalous osmose of solutions of electrolytes with collodion membranes. III. Effect of stirring solutions.** F. E. BARTELL AND D. C. CARPENTER. *J. Phys. Chem.* 27, 346-55(1923); cf. *C. A.* 17, 2072.—The investigation has been made to substantiate the hypothesis that the abnormal osmotic behavior of electrolytes is due to the passage of the solute through the membrane. Parallel sets of expts. have been run in one of which the solns. were stirred. The amt. of salt passing through the membrane was detd. by means of cond. measurements and the osmose rate in the same manner as in previous investigations. The amt. of solute passing through the membrane was greater in the stirred solns. The osmose rate at the same time was lowered. Irregularities in the osmotic behavior of the solns. were augmented by stirring. The rate of passage of the solute through the membrane is a function of the concn. of the soln. but is not proportional to it. The ratio of the concns. in the two compartments decreased as osmose progressed. The rate of passage is apparently a function of the valence, being slower the higher the valence, for the ions used.

C. R. PARK

**The precipitation of metals of the odd series of group II of the periodic system from their aqueous solutions by hydrogen at high pressures.** V. N. IPATZEV AND A. N. STARYNKOVITCH. *Bull. acad. sci. Russ.* 1918, 119-26.—The soln. pressure; of Cd and Zn, calcd. from Nernst's formula, are  $3 \times 10^4$  and  $10^{16}$  atm., resp.; hence the possibility of pptg. these metals by H even at high concns. seems improbable. To test this prediction a series of expts. was conducted in a special app. with the following results. All solns. were 2*N* except as otherwise noted, and pressures, temps., time and results are indicated. *HgNO<sub>3</sub>* (cold satd.): 100 atm., 160°, 13 hrs., crystals of a yellow basic salt and drops of Hg; 90 atm., 225°, 13 hrs., complete reduction to metal. *Hg(NO<sub>3</sub>)<sub>2</sub>* (cold satd.): 100 atm., 175°, 3 hrs., salt of Hg<sup>+</sup> but no reduction of HNO<sub>3</sub>; same except 213°, more basic salt and micro-inclusions of Hg; same except 245°, complete reduction to metal covered with red HgO. Traces of NH<sub>3</sub> were formed only above 200° and after 10-12 hrs. *Cd(NO<sub>3</sub>)<sub>2</sub>*: 110 atm., 180°, 7 hrs., no reaction; 135 atm., 220°, 7 hrs., small quantity of indefinite basic salt floating on soln.; 220 atm., 270°, 10 hrs., same salt plus well defined grayish hexagonal crystals of Cd. *CdSO<sub>4</sub>*: 250 atm., 270°, 7 hrs., hydrated sulfate in crystals and traces of Cd; prolonged heating produces crystals of CdS. *Zn(NO<sub>3</sub>)<sub>2</sub>*: atm., 290°, - hrs., basic salt; 320 atm., 340°, - hrs., transparent needles of ZnO with micro-inclusions of Zn. *ZnSO<sub>4</sub>*: 250 atm., 290°, 5 hrs., isotropic crystals of phosphorescent ZnS. *Mg(NO<sub>3</sub>)<sub>2</sub>*: 225 atm., 340°, 6 hrs., transparent crystals of Mg(OH)<sub>2</sub>. *MgSO<sub>4</sub>*: 330 atm., 350°, - hrs., MgS formed and hydrolyzed to Mg(OH)<sub>2</sub>. *HNO<sub>3</sub>* (sp. gr. 1.4): 250 atm., 340°, - hrs., NH<sub>4</sub>NO<sub>3</sub> + NH<sub>3</sub>. *H<sub>2</sub>SO<sub>4</sub>* (10%): 210 atm., 340°, - hrs., H<sub>2</sub>S. *KHCO<sub>2</sub>*(2*N*): 330 atm., 350°, 4 hrs., 11% K formate. M. G. KORSUNSKY

**Detection of the formation of complex salts in dilute solutions. II. Effects of concentration and solvent on the formation of complex salts.** YUJI SHIBATA AND TOSHI INOUE. *J. Chem. Soc. Japan* 43, 772-81(1922); cf. *C. A.* 16, 2075.—HgCl<sub>2</sub> and BaCl<sub>2</sub> were mixed in various ratios and the spectroscopic analysis of the mixt. was made at 10 mm. depth. The results show that in equimol. soln., the mixt. of the salts forms a complex salt within concns. of 0.1-0.0025 *M*. With 0.002 *M* there is no max. absorption, i. e., no complex-salt formation. If 0.0025 *M* soln. is used in a 5-mm. vessel, it shows max. absorption. If, however, 0.004 *M* soln. is dild. to twice that amt. and used in a 10-mm. vessel, there is no complex-salt formation. Thus the complex salt is totally decomposed in 0.002 *M* solns. The halides and thiocyanate of other metals do not change the structure of complex-salt function in dila., the effect of dila. being to shift absorption towards shorter wave lengths. The mol. ratios of each component with HgCl<sub>2</sub> and the minimum concn. at which complex salts are formed, are given for chlorides of Li, Na, K, NH<sub>4</sub>, Sr, Ba, Co, Al, Co(NH<sub>3</sub>)<sub>6</sub>; bromides of Na, K, NH<sub>4</sub>, Zn, Cd; iodide of Cd; and KSCN and Co(SCN)<sub>4</sub>. The structures of the complex salts are the same regardless of the concn. of the components, but at certain concns. these complex salts decompose completely. If monobasic halides are used, complex salts are formed up to 0.005 *M*, but decompose at 0.0025 *M*. With dibasic chlorides, they are stable up to 0.0025 *M*, but decompose at 0.002 *M*. With tribasic chlorides they are stable up to 0.002 *M*, but decompose at 0.00125 *M*. NaBr behaves about the same as the chloride. The other bromides and thiocyanates do not combine in equal mol. ratios and the stabilities of the complex salts extend to much lower concns. In alc. soln., in general the max. absorption occurs in the region of greater wave length. The results are given as follows for different salts in aq. and alc. solns., resp.: HgCl<sub>2</sub>-NH<sub>4</sub>Cl (0.01 *M*)

2563 Å., 2747 Å.;  $\text{HgCl}_2\text{-CoCl}_2$  (0.01 *M*) 2598 Å., 2731 Å.,  $\text{HgCl}_2\text{-CoCl}_2$  (0.0025 *M*) 2472 Å., 2625 Å.;  $\text{HgCl}_2\text{-MgCl}_2$  (0.0025 *M*) 2472 Å., 2625 Å.; and  $\text{HgCl}_2\text{-Co(SCN)}_4$  (0.001 *M*) 3058 Å., 3286 Å. The structures of the complex salts in alc. are the same as in aq. solns. The extent of diln. in alc. soln., without decompn. is greater than in  $\text{H}_2\text{O}$ . In alc. soln. monobasic chlorides are stable in 0.01 *M*, but decompose at 0.0005 *M*; and dibasic chlorides are still stable at 0.0005 *M*. S. T.

**Acid reaction of ammonium salts on litmus.** CAM. GILLET. *Bull. soc. chim. Belg.* 32, 178-9 (1923).—Blue litmus paper impregnated with a soln. of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{NO}_3$ , or  $(\text{NH}_4)_2\text{SO}_4$  turns red if dried and hung for some time in the air. This is not due to an oxidation, as assumed by C. Reichard (*Chem.-Ztg.* 1903, 1105), but simply to an evapn. of  $\text{NH}_3$ , as the same reaction takes place if the paper is dried in an atm. of  $\text{H}_2$ . R. BEUTNER

**Transference numbers of inconstant solutions over potassium chloride and sodium chloride.** EBERHARD KAYSER. *Kali* 17, 1-9, 37-42 (1923).—An address. The results of this study of const. or equally satd. and inconst. or unequally satd. solns. of  $\text{KCl}$  and  $\text{NaCl}$  are assembled in 18 tables and are illustrated by 20 charts of curves. L. W. RIGGS

**The transference numbers of sodium and potassium in mixed chloride solutions.** R. F. SCHNIEDER WITH S. A. BRALEY. *J. Am. Chem. Soc.* 45, 1121-34 (1923).—From the detn. of the transference numbers and transference ratios of Na and K in mixed chloride solns. as well as of the equiv. conductances the mobilities of the ions have been calcd. The results indicate that solns. are extremely complex and not in accord with the hypothesis of complete dissociation. The mobility of Na at a total concn. of 0.2 *N* and a ratio 3  $\text{KCl}$  : 1  $\text{NaCl}$  is practically zero. BENJAMIN S. NEUHAUSEN

**Conductivity of binary highly dissociated electrolytes.** W. MUND. *Bull. soc. chim. Belg.* 32, 156-78 (1923).—As an important further development Ghosh's theory of electrolytic dissociation (*C. A.* 12, 1609, 2268; 13, 88; 14, 3013, 15, 977, 3418) has been found to agree with the cond. measurements in the case of neutral salts, but not in the cases of strong acids and alkalies. M. recognizes that this discrepancy is due to the large difference of ionic mobilities and he devises an ingenious method for expressing this influence mathematically. Ghosh calcs. the work to be done for overcoming the electrostatic attraction of anion and cations ( $A$ ), expressing this magnitude (1) in terms of mol. cond. of the soln., (2) in terms of its concn. Since the 2 functions, are equal to each other, a relation is established between the mol. cond. and concn. M. follows the same principle, but assumes that the sp. cond. of a soln. is proportional to the ionic concn. in its surface (or on an electrode). This assumption includes the conception that the osmotic pressure in the surface may be lower than in the interior of the soln. owing to the lack of that mutual electrostatic attraction of the ions which acts in the interior. The sp. conductivity, then, would be  $\kappa = K\eta(p-\epsilon)/p$ , where  $K$  is a const.,  $\eta$  the diln.,  $p$  the osmotic pressure in the interior of the soln.,  $p-\epsilon$  the diminished osmotic pressure in the surface. The mol. cond.  $\lambda = \kappa/\eta$  would be equal to  $K(p-\epsilon)/p$ . Since  $\epsilon$  would be zero for infinite diln.,  $\lambda_{\infty} = K$ , or  $\lambda_{\infty}/\lambda = p/(p-\epsilon)$ . For calcg. the work of overcoming the ionic attraction ( $A$ ), one equiv. anion and one equiv. cation are to be transported from the interior into the surface; either transport corresponds to the work  $(RT/F)\ln p/(p-\epsilon)$ . The total work  $A$ , therefore, equals  $(2RT/F)\ln p/(p-\epsilon)$  or  $(2RT/F)\ln \lambda_{\infty}/\lambda$ , and is thus expressed in terms of mol. cond. If the anionic and cationic mobilities are not equal  $A$  must be expressed as  $(RT/F)\{\ln p/(p+\epsilon_1) + \ln p/(p+\epsilon_2)\}$   $\epsilon_1$  and  $\epsilon_2$  being the decrease of osmotic pressure from the interior to the surface for the anion and the cation, resp.  $A$ , in this case, is expressed in terms of mol. cond. as follows:  $A = (2RT/F)\ln\{\lambda_{\infty}(\sigma)/\lambda - \lambda_{\infty}(\sigma-1)(\gamma/\sigma)\}$ , where  $\sigma = K_1 + K_2/2\sqrt{K_1K_2}$ ;  $K_1$  and  $K_2$  being the anionic and the cationic mobilities,  $\sigma$  is the factor of asymmetry (which is 1 if  $K_1 = K_2$ ), and  $\gamma$  is another still more complicated function of the ionic mobilities. For practical application, however, M. assumes  $\gamma = \sigma$ . The formula, really applied is, therefore:  $A = (2RT/F)\ln \lambda_{\infty}/\sigma(\lambda - \lambda_{\infty}(\sigma-1))$ . The second part of M.'s calcn., viz. expressing  $A$  in terms of the concn. of the soln. is also based on the principles first introduced by Ghosh. However, while Ghosh reaches the result:  $A = \{(NE^2)/D\} \cdot \sqrt{2Nc}$ , M. finds  $A = 2.52/3 \cdot \{(NE^2)/D\} \sqrt{2Nc}$ , where  $N$  is Avogadro's no.,  $E$  the charge of one ion,  $D$  the dielec. const. of the soln., and  $c$  its concn. In deriving this modified formula, M. takes into account the forces of attraction and repulsion exerted on a single ion not only by one ion of the opposite charge, but by all ions of the opposite and the same charge which are in the neighborhood. By setting equal the 2 terms which express  $A$  as a function of the cond. and as a function of the concn., the final formula is derived, for calcg.  $\lambda$  at various concns. This is applied to the well

known cond. measurements of neutral salts, acids and bases at concns. ranging from  $10^{-3}$  to  $10^{-7}$ . With neutral salts M.'s new formula agrees slightly better with the observations than the one of Ghosh. With acids (*vis.* HCl and  $\text{HNO}_3$ ) and an alkali (*vis.* KOH), however, the agreement is very much better, principally because of the function of asymmetry introduced in M.'s calcul.

R. BRUTNER

Calculation of isoelectric points. P. A. LEVENE and HENRY S. SIMMS. *J. Biol. Chem.* 55, 801-13 (1923).—"The usual formula for single ampholytes,  $I = \sqrt{(K_a/K_b)} K_w$  =  $\sqrt{K_a k_b}$ , may be used to calc. the approx. isoelec. point of polyacidic, polybasic ampholytes without much error by using the  $K_a$  and  $K_b$  of the strongest acid and strongest basic group." ( $K_a$  = equil. const. of the acid,  $K_b$  = that of the base and  $K_w$  = that of  $\text{H}_2\text{O}$  at the temp. under consideration). The example adduced is aspartic acid, in which  $K_{a1} = 2.35 \cdot 10^{-4}$  and  $K_{a2} = 3.39 \cdot 10^{-10}$ . Defining the isoelec. point of a substance as that H-ion concn. at which it is ionized equally as an acid and as a base,  $\alpha_0 C + \alpha_1 C + \alpha_2 C + \dots \alpha_n C = \alpha_1 C + \alpha_2 C + \alpha_3 C + \dots + \alpha_n C$  or  $\Sigma \alpha_i C = \Sigma \alpha_j C$  or  $\Sigma \alpha_i = \Sigma \alpha_j$ . From the law of mass action for any monobasic acid  $K_a = (\text{H}^+) \alpha_0 / (1 - \alpha_0)$ ,  $\alpha_0 = K_a / (\text{H}^+ + K_a)$  and, similarly for a base,  $\alpha_n = K_b / [(\text{OH}^-) + K_b]$  or substituting  $K_w / (\text{H}^+)$  for  $(\text{OH}^-)$  and  $K_u / k_b$  for  $K_b$ ,  $\alpha_n = (\text{H}^+) / [(\text{H}^+) + k_b]$ ; therefore, at the isoelec. point,  $(A)$ ,  $(\text{H}^+) / [(\text{H}^+) + k_{b1}] + (\text{H}^+) / [(\text{H}^+) + k_{b2}] + \dots (\text{H}^+) / [(\text{H}^+) + k_{bn}] = K_{a1} / [(\text{H}^+) + K_{a1}] + K_{a2} / [(\text{H}^+) + K_{a2}] + \dots + K_{an} / [(\text{H}^+) + K_{an}]$ , or approx.  $(\text{H}^+) / k_{b1} + (\text{H}^+) / k_{b2} + \dots (\text{H}^+) / k_{bn} = K_{a1} / (\text{H}^+) + K_{a2} / (\text{H}^+) + \dots + K_{an} / (\text{H}^+)$ . From which,  $I = (\text{H}^+) = \sqrt{(K_{a1} + K_{a2} + \dots + K_{an}) / (1/k_{b1} + 1/k_{b2} + \dots + 1/k_{bn})} = \sqrt{K_w (K_{a1} + K_{a2} + \dots + K_{an}) / (K_{b1} + K_{b2} + \dots + K_{bn})}$ . This will give a value with a very small error and a more correct value can be obtained by substituting the value of  $(\text{H}^+)$  thus obtained in an expression derived from (A) above, which for the case of an ampholyte with 2 acid and 2 basic groups is given as  $I = \sqrt{(K_{a1} + K_{a2}) / (k_{b1} + k_{b2}) k_{b1} k_{b2} + K_{a1} K_{a2} [1 + (2k_{b1} k_{b2}) / (H(k_{b1} + k_{b2})) - H^2 / (k_{b1} + k_{b2}) (K_{a1} + K_{a2} + 2H)]}$  or  $= \sqrt{(K_{a1} + K_{a2}) / (K_{b1} + K_{b2}) K_w + K_{a1} K_{a2} [1 + 2K_w / H(K_{b1} + K_{b2})] - [H^2 K_{b1} K_{a1} / K_w (K_{b1} + K_{b2})] (K_{a1} + K_{a2} + 2H)}$ .

I. GREENWALD

The ionizing property of fused lithium hydride. A. GUNTZ and BENOIT. *Compt. rend.* 176, 970-1 (1923).—A deposit of C is formed at the anode when an elec. current is passed through  $\text{Li}_2\text{C}_2$  dissolved in fused LiH. With an e. m. f. above 0.1 v. H is set free at the anode; below 0.1 v. no H is liberated but at 0.05 v. a deposit of C is obtained. These expts. seem to indicate that  $\text{Li}_2\text{C}_2$  is ionized when dissolved in the fused hydride. The carbides of the alk. earth metals are also apparently ionized when dissolved in their molten hydrides.  $\text{CaC}_2$  dissolves without decompn. in a fused mixt. of LiCl and LiH. When electrolyzed this mixt. yields C at the anode. The nitrides of the alk. earth metals are sol. in the corresponding fused hydrides and seem to be similarly ionized.

L. T. FAIRHALL

Chemical reactivity. I. Mechanism of the formation of valerolactone. W. H. GARRETT and W. C. M. LEWIS. *J. Am. Chem. Soc.* 45, 1091-102 (1923).—The conversion of hydroxyvaleric acid into valerolactone under the catalytic influence of H ions is a bimol. process, the reaction being measured by the rate of effective collisions between the activated hydroxy-acid mols. and the H-ions. A characteristic bimol. const. is obtained at a given temp., which is not altered by change in catalyst concn. or by the presence of sucrose, KCl or LiCl in the reaction mixt. The effect of  $\text{H}_2\text{O}$  of hydration of sucrose and of KCl on the hydroxyvaleric acid mol. is quite different. The  $\text{H}_2\text{O}$  of hydration of the former is not available as solvent, whereas that of neutral salts is. The crit. increment of the reaction is 12,750 cal. per mol. of acid transformed.

H. JERMAIN CREIGHTON

Substitution factors of the affinity constants for the group of arsonic acids. RICHARD LORENZ and ELIZABETH BREHMER. *Ber.* 56B, 742-50 (1923).—The influence of substituents upon the affinity consts. of the carboxylic acids has been given by Wegscheider (*Wien. Akad. Ber.* 111, 67 (1902)) in the form of factors, whereby the affinity consts. of any acid may be found by multiplying the affinity const. of the original acid by the factor corresponding to the substituent. A similar table of factors for the arsonic acids shows that factors for  $\text{NO}_2$ , for OH, and for  $\text{CH}_3$  in the meta or para positions to the  $\text{AsO}(\text{OH})_2$  group are approx. the same for the two series of acids. Substitution in the ortho position gives wide differences between the two series of acids, the factor for  $\text{NO}_2$  being 103 for carboxylic acids and 1.5 for arsonic acids; the factor for OH is 17 for carboxylic acids and 0.42 for arsonic acids. Substitution of  $\text{NH}_2$  in the para position in arsonic acids gives a factor averaging 0.23, which cannot be compared with the other series.

JAMES M. BRILL

Some induced reactions. N. R. DHAR. *J. Proc. Asiatic Soc. Bengal, Proc. 8th Indian Sci. Cong.* 17, cxxx(1921); cf. *C. A.* 15, 3237.—A soln. of  $\text{HgCl}_2$  can be reduced by oxalic acid, tartaric acid, etc., in the dark only by the action of oxidizing agents like  $\text{KMnO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$ , etc. The oxidation of solns. of Na arsenite, Na formate, Na oxalate, Na nitrite and ferrous  $\text{NH}_4$  sulfate by atm. O can be induced by the simultaneous oxidation of  $\text{Na}_2\text{SO}_3$ ,  $\text{SnCl}_2$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{AcH}$ ,  $\text{CH}_3\text{O}$ ,  $\text{BzH}$ , etc., by air. The decompn. temp. of  $\text{KClO}_3$  is appreciably lowered by the presence of decomposing  $\text{NH}_4$  dichromate or persulfate. It seems probable that one chem. change will either induce or promote another chem. change of the same nature. In oxidation reactions, the phenomenon of negative catalysis is possible only when the negative catalyst is liable to be oxidized readily. A ferrous salt acts as an inductor in the reactions between  $\text{HgCl}_2$  and an oxalate or a tartrate or a citrate.

E. J. C.

Study of catalytic actions at solid surfaces. X. The interaction of carbon monoxide and hydrogen as conditioned by nickel at relatively low temperatures. A practical synthesis of methane. E. F. ARMSTRONG AND T. P. HILDRITCH. *Proc. Roy. Soc. (London)* 103A, 25-34(1923); cf. *C. A.* 17, 233.—The action between CO and  $\text{H}_2$  in the presence of Ni or a similar catalyst at temps. below  $300^\circ$  is mainly  $2\text{CO} + 2\text{H}_2 = \text{CO}_2 + \text{CH}_4$ . The reaction is considered to go in 2 stages; (1)  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ ; (2) the  $\text{H}_2$  so formed with that already present causes the formation of methane,  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ . No evidence was found for the intermediate formation of  $\text{CH}_3\text{O}$  or  $\text{MeOH}$ . Co is also quite active and the change commences at a lower temp. than with Ni. By this method the large amt. of CO in municipal gas supplies may be reduced and the content of  $\text{CH}_4$  increased. Pure  $\text{CH}_4$  may also be prepd. by passing water gas over Ni several times, removing  $\text{CO}_2$  from the gas each time, and fractionating the product at low temps.

JAMES M. BELL

Catalytic combination of ethylene and hydrogen in the presence of metallic copper. I. Measurements of reaction velocity and adsorption isotherms at  $0^\circ$  and  $20^\circ$ . R. N. PEASE. *J. Am. Chem. Soc.* 45, 1196-1210(1923).—The kinetics of the catalytic combination of  $\text{H}_2$  and  $\text{C}_2\text{H}_4$  have been studied at  $0^\circ$  and  $20^\circ$  in the presence of Cu. The reaction velocity and adsorption isotherms have been detd. Within limits the velocity increases with the  $\text{H}_2$  concn., but decreases as the  $\text{C}_2\text{H}_4$  concn. increases. The temp. coeff. of the reaction velocity per  $10^\circ$  rise between  $0^\circ$  and  $20^\circ$  is 1.62, indicating that diffusion does not play a dominant part.

H. JERMAIN CREIGHTON

Catalytic decomposition of hydrogen peroxide in a bromine-bromide solution, and a study of the steady state. WM. C. BRAY AND R. S. LIVINGSTON. *J. Am. Chem. Soc.* 45, 1251-71(1923).—Bromide is oxidized to Br and Br is reduced to bromide simultaneously and independently in the same soln. by  $\text{H}_2\text{O}_2$ . When the rates of these 2 compensating reactions are equal, a "steady state" ensues in which the concns. of Br, bromide and acid remain const., the net result being the catalytic decompn. of  $\text{H}_2\text{O}_2$ . At  $25^\circ$  in the dark in  $\text{H}_2\text{SO}_4$  soln., the rate of decompn. of  $\text{H}_2\text{O}_2$  is given by the expression,  $-d(\text{H}_2\text{O}_2)/dt = 0.0140(\text{H}_2\text{O}_2)(\text{acid})(\text{bromide})$ . At the steady state,  $(\text{Br})(\text{acid})^2(\text{bromide})^2 = R = 0.20$ . The value of  $R$  increases slightly as the temp. decreases, but decreases to a small value when the reaction mixt. is exposed to sunlight. It is shown that the catalysis of  $\text{H}_2\text{O}_2$  is accounted for by the 2 compensating reactions. The choice of catalysts based on free-energy data is discussed, and a method described for the volumetric detn. of  $\text{H}_2\text{O}_2$  in the presence of bromide.

H. J. C.

Ternary system, aluminium-zinc-tin. I. E. CREPAZ. *Giorn. chim. ind. applicata* 5, 115-22(1923).—Monograph, comprising the following topics: Zn-Sn system; Al-Sn system; e. m. f. of alloys of the binary systems; potential of Zn-Sn alloys; potential of Al-Sn alloys. Tables and curves showing the above properties are given.

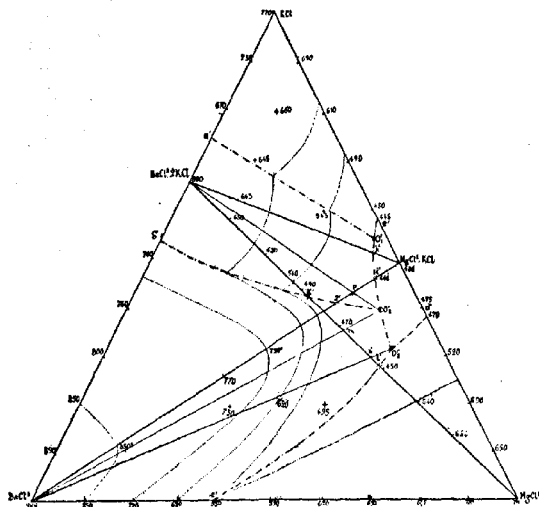
ROBERT S. POSMONTIER

The trajectories of crystallization in chemical equilibrium diagrams. N. S. KURNAKOV AND S. F. ZEMCHUZHII. *Bull. acad. sci. Russ.* 1918, 1855-8.—In connection with results obtained by other authors in exptl. work, covering the isothermic crystn. of the mutual system:  $2\text{NaCl} + \text{MgSO}_4 = \text{Na}_2\text{SO}_4 + \text{MgCl}_2$  from aq. solns. at  $25^\circ$ , it is stated that both the isothermic and isotonic diagrams of equil., together with all derived diagrams, representing the correlations between compn. and properties, may be considered as polyhedra to which the rule of Euler:  $\alpha_0(\text{corners}) - \alpha_1(\text{edges}) + \alpha_2(\text{faces}) - 2 = 0$ , is generally applicable. Polyhedra of this type can be reduced to an open complex tree by removing  $n$  lines, where  $n$  is equal  $\alpha_1 - \alpha_0 + 1$ , and this reduction may be pushed further until the simple tree of crystn. of 2 phases (or 2 salts) is left. They can also be projected upon the surface of a globe, by drawing lines from the center of the globe through the corners of the polyhedron. These axes form the invariants of each system, while the polyhedral systems projected by them can be treated by the

means theory of algebraic groups. It is pointed out that this case represents a remarkable correlation between the presentations of physical chemistry and pure algebra.

M. G. KORSUNSKY

**Solidification diagram for the system  $\text{MgCl}_2\text{--KCl--BaCl}_2$ .** C. MATIGNON AND J. VALENTIN. *Bull. soc. chim.* 33, 267–80 (1923).—This system is of interest because it can furnish an electrolyte for the electrolytic prepn. of Mg. The exptl. method consisted in the study of the cooling curves of the necessary mixts. The system  $\text{MgCl}_2\text{--KCl}$  gives 2 eutectics at  $470^\circ$  and  $440^\circ$  and one compd.,  $\text{MgCl}_2\cdot\text{KCl}$ . The system,  $\text{BaCl}_2\text{--MgCl}_2$  gives a eutectic at  $550^\circ$  for 36 mol. %  $\text{MgCl}_2$ . Three series of ternary mixts.



were then studied which were so chosen that they could be treated as binary mixts., resp., of (1)  $(\text{MgCl}_2\cdot\text{KCl})\text{--}(2\text{KCl}\cdot\text{BaCl}_2)$ ; (2)  $(\text{BaCl}_2)\text{--}(\text{MgCl}_2\cdot\text{KCl})$ ; and (3)  $(\text{BaCl}_2\cdot\text{KCl})\text{--}(\text{MgCl}_2)$ . The results are plotted in the triangular diagram.  $O_1$ ,  $O_2$  and  $O_3$  are triple points, the broken lines are lines of binary eutectics, the light, full lines are isothermals, and the heavy, full lines indicate the 3 series of mixts. studied. F. L. BROWNE

**Heterogeneous equilibria between the chlorides of calcium, magnesium, potassium, and their aqueous solutions.** I. WM. B. LEE AND A. C. EGBERTON. *J. Chem. Soc.* 123, 706–16 (1923).—The ternary system  $\text{CaCl}_2\text{--KCl--H}_2\text{O}$  at  $25^\circ$ . The soly. of KCl is relatively greatly depressed by the presence of a small concn. of  $\text{CaCl}_2$ , and as the latter increases the KCl content rapidly decreases until it attains the order of from 3 to 4% of KCl, after which further addn. of  $\text{CaCl}_2$  does not cause the percentage of KCl to alter appreciably. A very striking increase in the viscosity of the satd. solns. occurs as the content of  $\text{CaCl}_2$  increases until at the break-point the viscosity is over 20 times that of water. The ternary system  $\text{CaCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$  at  $25^\circ$ . Besides the 2 hydrates,  $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ , the double salt, tachhydrite,  $\text{CaCl}_2\cdot 2\text{MgCl}_2\cdot 12\text{H}_2\text{O}$  occurs as a solid phase. The ternary system  $\text{MgCl}_2\text{--KCl--H}_2\text{O}$  at  $25^\circ$ . The solid phases which appear at  $25^\circ$  are KCl,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  and carnallite. JAMES M. BELL

**System, calcium oxide-carbon dioxide.** F. H. SMYTH AND L. H. ADAMS. *J. Am. Chem. Soc.* 45, 1167–84 (1923).—Equil. pressures have been detd for the system  $\text{CaO--CO}_2$ , which define it experimentally from 587 to  $1339^\circ$ , and from 0.1 to 779,000 mm. pressure. Up to the eutectic point the temp.-pressure relations of the system  $\text{CaCO}_3\text{--CO}_2$  are given by the expression:  $dp/dt = p(2.3026 \times 11,355/T^2) - 5.388/T$ . The m. p. of  $\text{CaCO}_3$  contg. only 0.38% CaO is  $1339^\circ$  at 779,000 mm. pressure. The eutectic between  $\text{CaCO}_3$  and CaO lies at  $1240 \pm 1^\circ$  and  $30,000 \pm 300$  mm., the compn. being

about 50% of each component. Only one cryst. form of  $\text{CaCO}_3$  exists with in the temp. range studied.

H. JERMAIN CREIGHTON

The exposed stem correction for mercury thermometers. WM. L. DE BAUFRE. *Power* 57, 320-1(1923).—Diagrams are given by which stem corrections for thermometers can be made.

D. B. DILL

Determination of the temperature of combustion. F. POLLITZER. *Z. angew. Chem.* 35, 683-5(1922).—P. presents a graphic method for detg. the max. theoretical temp. of combustion. He obtains the max. temp. of the reaction  $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$  by plotting against temp. the values for the increase in energy content of  $\text{CO}_2$  with increasing temp. and noting the temp. at which the increase in energy content is equal to the heat of reaction. The presence of indifferent gases or an excess of one of the reacting gases lowers the max. temp. The temp. is also influenced by the dissociation of the products of the reaction. P. detd. the max. temp. of several reactions, taking into account the effect of the dissociation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The values thus obtained are compared with those of Bronn (*Z. angew. Chem.* 35, 328(1922)) and shown to be lower.

L. M. HENDERSON

The temperature variations of the heats of solution. PAUL MONDAIN-MONVAL. *Compt. rend.* 176, 889-92.—The author measures exptly. (1) the heat of soln. in much water,  $Q$ ; (2) the heat of diln.,  $D$ , of a satd. soln. dild. to the condition corresponding to  $Q$ ; (3) the heat produced by adding a small amt. of water to a large vol. of satd. soln., reduced to the amt. of added water sufficient to dissolve 1 mol. at satn.,  $\epsilon$ . Then  $L$ , the heat produced by dissolving the last mol. of salt to make a large amt. of satd. soln. is related to the above quantities as follows:  $L_1 = Q - D - \epsilon$ . As a check,  $L$  was independently and exptly detd. by extrapolation of the results obtained by dissolving the salt directly in solus. more and more concd., and found to agree to 2% or better. The work on 6 salts was done in vacuum-jacketed calorimeters at 2 temps., one of which was  $0^\circ$ . The essential results follow, all values being negative.  $\text{NaNO}_3$ , at temps., resp.,  $0^\circ$  and  $16^\circ$ :  $Q$  5.25, 4.75;  $D$  2.57, 2.02;  $\epsilon$  0.745, 0.58;  $L_1$  1.94, 2.15;  $L$  1.97, 2.13.  $\text{KCl}$ , temps.  $0^\circ$  and  $18^\circ$ :  $Q$  5.01, 4.27;  $D$  0.95, 0.59;  $\epsilon$  0.57, 0.465;  $L_1$  3.49, 3.22;  $L$  3.5, 3.25.  $\text{NH}_4\text{NO}_3$ , temps.  $0^\circ$  and  $19^\circ$ :  $Q$  6.48, 6.2;  $D$  2.7, 2.5;  $\epsilon$  0.79, 0.65;  $L_1$  2.99, 3.05;  $L$  3.04, 3.06.  $\text{NH}_4\text{Cl}$ , temps.  $0^\circ$  and  $19^\circ$ :  $Q$  4.06, 3.84;  $D$  0.414, 0.155;  $\epsilon$  0.278, 0.123;  $L_1$  3.37, 3.56;  $L$  3.30, 3.58.  $\text{KNO}_3$ , temps.  $0^\circ$  and  $18^\circ$ :  $Q$  8.8, 8.3;  $D$  1.47, 1.71;  $\epsilon$  0.87, 1.14;  $L_1$  6.45, 5.45;  $L$  6.4, 5.6.  $\text{K}_2\text{SO}_4$ , temps.  $0^\circ$  and  $18^\circ$ :  $Q$  8.02, 6.4;  $D$  0.87(?), 0.67(?);  $\epsilon$  0.54(?), 0.57(?);  $L_1$  6.62(?), 5.2(?);  $L$  6.75, 5.9.

W. P. WHITE

Oscillations of temperature of an incandescent filament, and the specific heat of tungsten. K. K. SMITH AND P. W. BIGLER. *Phys. Rev.* 19, 268-70(1922).—A study of thermionic currents for recording rapid changes in the temp. of a filament. By a double high-frequency oscillograph, continuous photographic records were obtained of cyclic variations in thermionic emission for a W filament *in vacuo* and of the variations in the alternating voltage. By having a sufficiently high const. potential difference between filament and anode, variations in the thermionic current were caused only by temp. changes. The change in the mean thermionic current from a known temp. change was converted, by measuring the photographic variations, into oscillations above and below the mean temp. By means of the theoretical relation between the oscillation in temp. and heat capacity of W as deduced by Corbino (cf. *Physik. Z.* 11, 413(1910)) and the mean temp. of the filament as calcd. by Langmuir (cf. *C. A.* 10, 1298), the *at. heat of W* at const. pressure was calcd. to be 8.75 cal. per g. atom per degree (cf. *C. A.* 12, 1432).

C. C. DAVIS

The heat of vaporization and the difference of the specific heats at saturation for neon. F. MATHIAS, C. A. CROMMELIN ONNES, and H. KAMERLINGH ONNES. *Compt. rend.* 176, 939-40(1923).—This extends a previous research (*C. A.* 16, 4120). The vapor pressure of Ne, derived from expt., is:  $\log p = -(84.3796/T) + 2.81911 + 0.01118 T$ . The latent heat  $L$  is calcd. from  $L^2 = 43.56922 (T_c - T) - 1.74434 T (T_c - T)^2 + 0.0371203 (T_c - T)^3$ , where  $T_c$  is the abs. crit. temp. The diff. of sp. hts.,  $m' - m$  is  $(dL/dT) - (L/T)$ . It is always negative. Since Ne is monatomic  $m'$  is always negative. The crit. temps. and heats of vaporization are also given for O, Ar, N, Ne, and H.

W. P. WHITE

The heat of fusion of camphor. N. N. EFREMOV. *Bull. acad. sci. Russ.* 1919, 765-76.—The heat of fusion of camphor,  $W$ , is calcd. from the formula  $W = 0.2 \times T^2/\Delta t \times M = 8.39 \text{ cal./g.}$ , where  $T$ , the abs. temp. of fusion =  $451^\circ$ ,  $M = 152$ , and  $\Delta t$ , the av. exptl. value for the f. p. depression of 22 org. compds. dissolved in camphor, = 3.19. The above value of  $W$  agrees well with that (8.35) calcd. from the temp. factor of vapor pressure.

M. G. KORSUNSKY

A new tendency in physical chemistry. J. BIKERMAN. *Rev. gen. sci.* 34, 197-201

(1923).—General discussion of the increasing use of Coulomb's law and thermodynamics, particularly as exemplified in the theory of Ghosh, to explain numerous phenomena such as abnormalities in colligative properties, which were formerly attributed upon the basis of Avogadro's hypothesis to association, polymerization, electrolytic dissociation or changes in the no. of mols.

G. L. CLARK

**Overvoltage. I. Hydrogen overvoltage.** TADASHI ONODA. *J. Chem. Soc. (Japan)* 43, 491-534 (1922).—The over-voltage was measured by the "bubble method" with an arrangement somewhat similar to that of Thiel. Four different metals were studied. (1) Au. Pt electrodes, plated with Au by 2 different methods showed no different over-voltage. The reproducibility of the electrode, however, does depend on its subsequent history after plating. A newly prep'd. electrode gave 0.0162 v.; this rose to 0.0238 v. after 1 day's exposure in air, to 0.0293 v. after 2 days and to a max. value (10 times that of the initial v.) after 10 days. Various mediums ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{AcOH}$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{H}_2\text{O}$  and  $\text{NaOH}$ ) other than air were also used but in no case were the initial values retained. A particular method was discovered by which any electrode will give a const. min. over-voltage. It is as follows. The electrode is treated anodically in the soln. till just a few bubbles begin to collect, washed and then treated cathodically in the app. for a little longer time than the anodic treatment. By this method the min. over-voltages may be obtained from all electrodes kept in the different conditions which had different over-voltages at the different times. The min. over-voltage for Au ( $20^\circ$ ) is 0.0086 v. The values given by Thiel and Breuning correspond to that obtained by O. with a newly prep'd. electrode; by Casper, to that with a day-old electrode; and by Cohen and Cannenberg as well as by Müller to those with electrodes exposed several days to air or in a soln. The various other factors which influence over-voltages are also given. (2) Cu. The min. over-voltage of Cu at  $20^\circ$  is 0.0977 v., while the newly prep'd. electrode gives 0.13. (3) Pt. A platinized Pt electrode should theoretically give zero, but showed 0.0008 to 0.001 v. at  $20^\circ$ . If the platinizing fluid contains Pb, it gives 0.0054 v. A Pt plate electrode gives 0.0063 v. (4) Ni has a min. of 0.0869 v. at  $20^\circ$ , while a new electrode gives 0.1 v. Over-voltage varies practically directly proportionally to temp. The temp. coeffs. of min. over-voltages are: Pt plate electrode,  $-14 \times 10^{-6}$  v.; Au,  $-32 \times 10^{-6}$  v.; Cu,  $-456 \times 10^{-8}$  v.; and Ni,  $-480 \times 10^{-6}$  v. **II. Oxygen overvoltage.** *Ibid* 782-809.—The general arrangement of app. is about the same as above. The results show that O over-voltages of different electrodes undergo practically no change after prep'n. The reverse (cathodic-anodic) treatment used for obtaining H min. over-voltage (anodic-cathodic, see previous abst.), does not give different values. At  $20^\circ$ , nickelized Ni electrode gives 1.3992, Ni plate 1.405 v., platinized Pt 1.4412, Cu 1.4652, Pt plate 1.663 v., and Au 1.693 v. O over-voltages against a platinized Pt electrode are: nickelized Ni,  $-0.042$  v.; Ni plate  $-0.036$  v.; platinized Pt, 0 v.; Cu,  $+0.024$  v.; Pt plate  $+0.222$  v.; and Au,  $+0.252$  v. The effect of temp. is: for Pt,  $\pi_1 = 1.7355 - 0.0045 t$ ; Au  $\pi_1 = 1.7664 - 0.00388 t$ ; Ni  $\pi_1 = 1.3880 + 0.0019 t - 0.000039 t^2$ ; platinized Pt and nickelized Ni, exceedingly small.

S. T.

**Absolute null-point of electric potential.** SVEN BODFORS. *Z. Elektrochem.* 29, 121-3 (1923).—A new det'n. has been made of the potential of the calomel electrode, by a modified form of the method employed by Christiansen (Drud, *Ann.* 12, 1072). This consists in studying the movement of a drop of Hg in an electrolyte under a fall in potential. The drop of Hg moves towards the positive or negative electrode, depending on the Hg-ion concn. of the soln. The tube carrying the drop of Hg is directly connected to a N calomel electrode. A 0.1 N soln. of  $\text{KNO}_3$  and  $\text{NaNO}_3$  (86 mol. %  $\text{KNO}_3$ ) was used as the electrolyte, and to this was added a small quantity of  $\text{Hg}(\text{CN})_2$  to give a definite Hg-ion concn. The soln. was shaken with metallic Hg. To this soln. varying amts. of KCN were added, and the direction of the movement of the drop of Hg was observed. The results of the expts. show that the charge on the drop of Hg changes from positive to negative at  $-0.40 \pm 0.02$  v., i. e., if the drop of Hg is actually without elec. charge the abs. potential of the N calomel electrode is  $+0.40$  v. This value is considerably lower than that ( $+0.57$  v.) det'd. by Palmaer (cf. C. A. 1, 2527) for the 0.1 N calomel electrode.

H. JERMAIN CREIGHTON

**The polarization of electrodes.** J. E. VERSCHAFFELT. *Rec. trav. chim.* 41, 764-77 (1922).—V. has previously published (*Bull. acad. roy. Belg., classe des sciences* 1919, 441) a paper on this subject in which the statements of Aten (*Verslag Akad. Wetensch. Amsterdam* 25, 325 (1916)) based on Nernst's ideas are corrected. Since this statement was not included in the 1922 edition of Forster's *Elektrochemie wässriger Lösungen*, V. has now extended and revised his earlier statement. V. considers the fundamental phenomenon of the production of a elec. current between 2 electrodes of the same metal



that are plunged into a soln. of a salt of the metal and between which a p. d. is established. At the moment of application of the e. m. f.  $E$  there is established between the electrodes, which are supposed to be plane, parallel and very large in relation to their distance  $l$ , an electric field of intensity  $E/l$ . In this field the anions are displaced toward the anode and since they are not pptd. they accumulate there, and as they are not formed again (assuming the salt to be entirely dissociated) the cathode region becomes rarefied. The cations themselves are displaced toward the cathode, where they ppt. themselves in a measure detd. by the current intensity. At the interior of the soln. the current is only partly transported by the cations; the transport of the cations there is less intense than near the cathode so that on the cathode side the cations ought to become rarefied; on the other hand some cations enter soln. at the anode. The cations ought now also to accumulate on the anode side. Thus the establishment of the p. d.  $E$  between the electrodes has the effect of producing a fall of concn. in the entire liquid, from anode to cathode, of cations as well as anions. These 2 falls of concn. are not independent of each other: they are equal, or nearly so, when expressed in gram-equivs. because by virtue of the relatively enormous charges carried by the ions these differences in concn. of the 2 ions even when small, create elec. fields, and these produce currents that instantly equalize the concns. of the cations and anions. For this reason in treating this problem it is necessary to consider but one concn.  $c$ : this decreases from the anode to the cathode; and the fall in concn. zero at first, increases with the time until a stationary condition is established. These changes in the concn. at the electrodes are accompanied by changes of potential of the electrodes against the layers of the soln. with which they are in contact; the electrodes polarize themselves, while the potential of the cathode becomes more negative, and that of the anode more positive; the potential difference in the liquid is diminished but not annulled. Moreover this polarization of electrodes has not at first a detd. value: it varies gradually with the concn. at the electrodes, i. e., it passes continually from zero to a max. value, attained when the stationary state is established. The major part of the paper consists of a mathematical discussion of the problem.

E. J. WITZEMANN

Graphs for calculation of electron emission from tungsten, thoriated tungsten, molybdenum and tantalum. SAUL DUSHMAN AND J. W. EWALD. *Gen. Elec. Rev.* 26, 154-60 (1923); cf. *Phys. Rev.* 20, 109 (1922).—A series of graphs of the equation  $\log I = 1.7792 + 2 \log T - b_0/2.303T$  is given, in which  $\log I$  is plotted as ordinate against  $b_0$  at const. value of  $T$ . Values of  $b_0$  for W, Mo, Ta, Th, and Ca arc, resp., 52,600, 50,000, 46,500, 34,100 and 26,000. Corrections for the cooling effect of the leads and for the "Schottky effect" are discussed.

D. MACRAE

The sparking potential in argon at reduced pressures. E. R. STORKER. *Phys. Rev.* 19, 258-9 (1922).—The potential required to start an arc between Ca electrodes in A at 40 mm. pressure decreased progressively from 300 v. to 90 v., probably because of purification of the A by Ca vapor and of chem. action between the electrodes and traces of O or other gases, with emission of electrons. The sparking potential of A was then detd. by first purifying it by a Ca discharge and by CO<sub>2</sub> snow and sparking between brass electrodes. With  $p$  = pressure (mm. of Hg) and  $d$  = mm. distance between electrodes, a min. sparking potential of 176 v. was found for  $pd = 8$  with unpurified A, and 137 v. for  $pd = 7$  with A purified by the Ca arc. Still purer A should give lower values. Entrance of air bubbles changed the pressure approx. 1% and the sparking potential 7.5%.

C. C. DAVIS

Further experiments with liquid helium. Q. The electric resistance of pure metals, etc. X. Measurements concerning the electric resistance of thallium in the temperature field of liquid helium. H. KAMERLINGH ONNES AND W. TUYN. *Proc. Acad. Sci. Amsterdam* 25, 443-50 (1923); cf. C. A. 10, 308.—TI becomes superconducting at 2.32° K. R. The electric resistance of pure metals, etc. XI. Measurements concerning the electric resistance of ordinary lead and of uranium lead below 14° K. *Ibid* 451-7.—"Kahlbaum" lead (at. wt. 207.20) and uranium lead (at. wt. 206.06) become superconductors at the same temp., 7.2° K.

E. D. WILLIAMSON

The law of magnetic rotation. HAWKSWORTH COLLINS. *Chem. News* 126, 197-200 (1923).—Numerous calcs. are based on the generalization that the magnetic rotation of an electropositive element when in combination is the product of  $1/2$  its at. wt. and the reciprocal of its relative vol. (cf. C. A. 16, 4122). The calcd. values for magnetic rotation agree closely with the observed values.

JAMES M. BELL

Recent determinations of the susceptibilities of oxygen and nitric oxide and the magneton. E. C. FRIRTS. *Phys. Rev.* 19, 247-8 (1922).—A review of the work of Pauli (cf. C. A. 15, 628), Piccard (cf. C. A. 15, 2773) and of Soué (cf. C. A. 14, 375, 1923, 2746).

C. C. DAVIS

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## 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Whitaker's quantum mechanism in the atom. H. A. LORENTZ. *Proc. Acad. Sci. Amsterdam* 25, 414-22(1923).—A short mathematical article suggesting extensions of W.'s ideas about the action between an atom and an electron. E. D. W.

Positive-ray analysis of lithium and zinc. A. J. DEMPSTER. *Phys. Rev.* 19, 271 (1922).—Preliminary announcement of the isotopes 6 and 7 of Li, and of 3 strong components 2 units apart and 1 weaker on the heavy side in Zn. G. L. CLARK

Positive-ray analysis of zinc and calcium. A. J. DEMPSTER. *Phys. Rev.* 19, 431 (1922).—Further expts. with Zn have shown that large variations occur in the proportions of the 4 components observed (cf. *C. A.* 17, 673). This makes the reasoning invalid in which the at. wts. were deduced to be 63, 65, 67 and 69, in order that the mean wt. might agree with the chem. at. wt. 65.4. With Ca anodes to which a little Zn had been added, it was found possible to obtain the Ca and Zn lines at the same time and compare their at. wts. The Zn lines were thus found to have the at. wts. 64, 66, 68 and 70. This

makes Zn agree with the rule observed to hold in the isotopes of the inert gases, that even at. wt. usually goes with even at. no. The strong Ca line at 40 was compared with a K line at 39 and Mg line at 24. With Ca a weak component was observed with at. wt. 44. This is provisionally considered to be a real isotope and not due to  $\text{CO}_2$ , since any  $\text{CaCO}_3$  present should be dissociated at a lower temp. than that used. W. F. MEGGERS

**The classification and the prediction of isotopes.** W. D. HARKINS. *Phys. Rev.* 19, 252-3(1922).—In the equation  $P = 2(M + f)$  previously developed by H. and Wilson,  $f$  is the no. of cementing electrons for all atoms with atomic wt. divisible by 4. The values of  $2f$  are more suited as a basis of a system of classification, since they include only every whole no. from 0 to 57 if only complex nuclei are considered. The no.  $2f$  may be termed the isotopic no. ( $n$ ). Atoms may be classified also according to this disintegration or aggregation series. C. C. DAVIS

**The quantum theory and isotopes.** J. W. NICHOLSON. *Phil. Mag.* 45, 801-17 (1923).—Some miscellaneous calcns. in regard to the application of the quantum theory to at. structure and the question of isotopes. The so-called "pendulum" or straight-line path of an electron in an atom or mol. is first discussed. The case of the passage of an electron through the nucleus is dealt with and it is concluded that if it is physically possible, the path is a special case presenting no difficulties such as infinite velocity. The velocity would be that of light. Nuclear structure is discussed for the theoretical isotope of H with a nucleus of 2 protons and 1 electron. The possible differences of the spectra of isotopes are dealt with on 2 different bases. The effects due to difference in mass of the nucleus would be much larger for light than for heavy atoms. For the 2 Li isotopes it would be about 0.087 Å., for Pb 0.00006 Å. the order of magnitude found by Merton. General conditions regarding complex nuclei are adverse to the theory of heavy nuclei made up entirely of H and electrons. S. C. LIND

**Phase relations in Bohr's model of atoms and molecules.** M. BORN AND W. HEISENBERG. *Z. Physik* 14, 44-55(1923).—The application of quantum conditions to the motion of the electrons of 2 atoms leads to the conclusion that definite phase relations arise out of their reciprocal action. Such phase relations also exist between the motions of the electrons of the same atom. B. and H. conclude on the basis of their investigations that in the normal atom, the whole system of electronic paths is exactly in phase. The investigation is confined to the simple cases in which it is possible to see that there is no decrease in the number of phase integrals to be quantized. The mathematical method of Poincaré and Lindsteal, adapted to the quantum theory by Born and Pauli, was used. The method is insufficient for this problem and the necessary extension has been made by the application of Bohlén's method. The analysis cannot be condensed into an abstract. A. W. S.

**Experiments on the distribution of the active deposit from radium emanation under the action of an electric field.** G. CARRIÈRE. *Bull. soc. chim. Belg.* 32, 5-18 (1923).—Continuing the investigations of Schmidt (*C. A.* 2, 2494) and Mund (*C. A.* 16, 2256), C. measures the distribution of the decompn. products of Ra emanation in an elec. field by means of an improved app. The measurements are made in an atm. of dry air, of moist air, of dry  $\text{H}_2$  and of air charged with naphthalene vapors. The work will be continued and a discussion of the results is to be given later. R. BEUTNER

**The number of ions produced by  $\alpha$ -particles from radium C.** H. FONOVIČ-SMEREKER. *Sitz. Akad. Wiss., Wien, Abt. II* 131A, 355-63(1923).—Because of lack of agreement among the observations on the number of ions produced by an  $\alpha$ -particle, a direct detn. of this number was made for the  $\alpha$ -particles from Ra C. The method consisted in detg. the satn. current from a metal foil activated with RaC and then detg. the Ra equiv. of the foil by comparison with a Ra standard. The specimen to be studied was prepd. by exposing one side of a gold foil 1 cm. in diam. to Ra emanation, thus activating it with Ra C. The satn. current was measured after the  $\alpha$ -rays from Ra A caused no further error. The necessary corrections for the decay of the activity were made and the satn. value of the current was obtained by extrapolation. Correction was also made for the current due to the  $\beta$ -rays. This correction was detd. directly. The mean of fifteen series of measurements gave  $n = 2.20 \pm 0.02 \times 10^4$  as the number of ions produced in air by an  $\alpha$ -particle from Ra C. This value is about 7% less than the value  $n = 2.37 \times 10^4$  found by Geiger. By means of Geiger's formula a calcn. was made of the no. of ions produced by an  $\alpha$ -particle from each of the radioactive substances. A. W. SMITH

**The charge on the alpha particle.** J. E. SHRADER. *Phys. Rev.* 19, 422-3(1922).—The charge on the  $\alpha$ -particle was detd. by the methods of Rutherford and Geiger, with Po as radioactive source. The current was detd. by the null method with a quadrant

electrometer of 0.2% accuracy. Counting entailed an error of 4-5%, which is probably inherent in the sensitive point method, since the no. of particles does not agree with the inverse ratio of distance and varies disproportionately with the rate of decay. The entrance of an  $\alpha$ -particle produces a minute current by collision and ionization. This causes the release of ionized gas mols. from the point, and this source of ions rather than ionization by collision causes the greater part of the current. The irregularity of counting is due to instability of the gas film. The av. of detns. of currents due to positive charges of  $\alpha$ -particles and the no. of particles from the same source at different rates of counting gave  $e = 4.78 \times 10^{-10}$  E. S. units. C. C. DAVIS

**The effective range of  $\beta$ -rays.** J. A. GRAY AND A. V. DOUGLAS. *Phys. Rev.* 19, 432-3(1922).—This range has been obtained by using an electroscope to give a measure of the intensity of the  $\beta$ -rays. The source of  $\beta$ -rays was an active prepn. of Ra D + E. The effective range of these  $\beta$ -rays has been found in paper, Al, Cu, S and Pb. In paper the range is 0.47 g., in Pb 0.34 g., the range being inversely proportional to what has been called the mass absorption coeff. of the  $\beta$ -rays. W. F. MEGGERS

**High-frequency rays in the  $\gamma$ -ray spectrum of radium B and C.** A. F. KOVARIK. *Phys. Rev.* 19, 433(1922).—The source of the radiations was a standard Ra salt of 1.3 mg. Ra content. The Ra was placed in the center of a Pb block 15 cm. on the edge and the rays passed through an opening in this block and through a slit 1 mm. wide and 6 cm. deep in another block of Pb placed in front of the former. The rays fell on a crystal of calcite and were reflected into a point discharge counting chamber after passing through a slit 0.5 mm. wide and 7 cm. deep placed in front of the counting chamber. The counting chamber was also surrounded by Pb. The crystal and the counting chamber were moved together, the latter through double the angle of the former and the discharges produced in the counting chamber by the  $\gamma$ -rays entering through the slit (and otherwise) were automatically registered. The principal lines recorded by Rutherford were verified but other lines were also detected. Among these, it is of especial interest to note that there are at least five and possibly more lines of shorter wave-length than the shortest one reported by Rutherford and Andrade. W. F. MEGGERS

**Speculation concerning the positive electron.** H. H. POOLE. *Nature* 111, 15-6 (1923).—Lodge's speculation (*C. A.* 17, 679) is examd. from the point of view of the relative abundance of the lighter and heavier elements, H being considered in particular. An immense discrepancy is apparent. Doubtless, some negative protons would combine with previously formed positive complexes, but since about half the complex nuclei first formed would be negative, so that some of the positive protons would be lost by combination with them, these effects would be expected to balance approx. If, however, it is assumed that when two unequal nuclei combine, the sign of the combination is detd. by that of the larger constituent, it is conceivable that if the first set of nuclei formed happened to be positive, they might so direct the course of subsequent events as to lead to the existing distribution of the elements. J. C. S.

**Critical potentials of thallium vapor.** F. L. MOHLER, P. D. FOOTE AND A. E. RUARK. *Science* 57, 475-7(1923); cf. *C. A.* 13, 929.—In a previous article, 7.3 v. was reported as the ionization potential of Tl vapor. A careful repetition of the work gave  $6.04 \pm 0.1$  v., in good agreement with the new Bohr theory for the wave no.  $2p_1 = 49264$ , corresponding to 6.08 v. A discussion of the resonance potentials of Tl is included. Inspection of the previously reported data gave a value of 6.12 v. The ionization and resonance potentials for the other elements in the Al subgroup are predicted and recorded in a table. D. C. BARDWELL

**The quantum theory of the simple Zeeman effect.** A. M. MOSHARRAFA. *Proc. Roy. Soc. (London)* 102A, 520-37(1923).—A theory of the simple Zeeman effect is put forward. This theory has the same general features as the corresponding one of Epstein and Schwarzschild for the Stark effect. It is assumed that the steady states of the atom are governed by classical dynamics subject to quantum restrictions which hold both in the absence and the presence of the magnetic field. It is further assumed that radiation occurs during transitions from one steady state to another according to the relation,  $w_2 - w_1 = h\nu$ . The theory differs from the Bohr-Sommerfeld theory in the fact that in that theory the motion of the atom in the presence and in the absence of the magnetic field is not defined by classical dynamics but this assumption plays a fundamental role in the present theory. The quantum restrictions which define the steady state of the atom are not used in the original form proposed by Wilson but in a slightly extended form which was also proposed by Wilson. If the original form of the quantum restrictions is maintained both in the presence and in the absence of the magnetic field there is no difference between the energies of the corresponding static paths in the two cases and hence no theoretical reason for a resolution of the spectral lines. The ex-

tended form of the quantum restrictions, however, leads to the ordinary fine structure of the spectral lines. The magnetic field splits up each component of the fine structural group into a simple Zeeman triplet.

A. W. SMITH

**Researches on the luminescence of mercury vapors under the action of low-velocity electrons.** V. I. PAVLOV. *Bull. acad. sci. Russie* 1918, 127-50.—P. studied the visible luminescence of Hg vapors under normal pressure and temp. in a space free of electrical field action and under a const. flux of electrons of a definite velocity, as thrown out by a Wehnelt cathode. The minimum e. m. f. necessary for the visible luminescence was found to be 8.25 v. A series of expts. was performed with the aim of studying the spectrum of Hg vapor luminescence at the lower and the higher limits of electronic velocities. It was found that a definite amt. of electronic energy is needed for the excitation of each line of these spectra. Thus 8.25 v. were necessary to produce the green line of  $546\mu$ , while 11.75 v. produced the double yellow line of  $576.9-579.0\mu$ . Another series of expts. was undertaken to establish the optimum conditions for studying the mechanism of this luminescence in the most simple and controllable way. It was found that a min. volumetric density of the elec. energy of the discharge was necessary to start a visible luminescence. To increase the vol. of the luminous space, either an increase in the quantity of the electrons at a const. velocity, or an increase in velocity at a const. quantity is necessary. The loss of energy of electrons upon their impact with the atoms of Hg was clearly shown, together with the possibility of restoring this loss from the energy of an independent elec. field. An artificially striated luminescence was produced.

M. G. KORSUNSKY

**The relation between the visible luminescence and the ionization of mercury vapor under the action of electrons.** V. I. PAVLOV. *Bull. acad. sci. Russ.* 1918, 1931-54.—The increase of the initial ionization by the action of the field of elec. discharge (secondary ionization) does not present an indispensable part of the luminous discharge. It can be totally suppressed, without influencing the increase of ionization in the field of the visible luminescence. A variation in the initial ionization as brought about by different means, though necessary to start a visible luminescence and anomalously to ionize the gas, is not necessary for maintaining the luminosity. A const. mechanism of ionization of a gas may produce a quite different degree of ionization, after the first stage of luminescence is reached, when all ionizers develop a far larger efficiency. A "working" hypothesis concerning the cause of the latter phenomenon was developed.

M. G. KORSUNSKY

**A theory of electrodeless discharge in gases.** P. P. LAZAREV. *Bull. acad. sci. Russ.* 1919, 127-32.—Ionization of gases enclosed in electrodeless receptacles and placed in a suitable electromagnetic field can be regarded analogously to the gas-ionization in the field of light, which immediately precedes photochem. reaction. This leads L. to develop the quant. laws of the electrodeless discharge along the lines given in his theory of the photochem. process of vision (*Pflueger's Arch.* 154, 459(1913); cf. *C. A.* 8, 1288). The momentary velocity of ionization in a field of the const. av. intensity  $J$  must be  $dn_1/dt = \alpha_1 JN$ , where  $N$  is the momentary value of the non-ionized gas concn. This velocity is lowered by a reversed process of molecule formation and ion adsorption by the walls of the receptacle, so that  $-dn_1/dt = f(N_1)$ . Supposing the latter reaction to be of the monomol. type, and the initial concn. of gas equal  $N_0$ , an equation:  $(dn_1/dt) + (\alpha_2 + \alpha_1 J)N_1 = \alpha_1 N_0 J$  is obtained, and if the initial ionization is zero, this equation integrates to:  $N_1 = \{\alpha_1 N_0 J / (\alpha_2 + \alpha_1 J)\} [1 - e^{-(\alpha_2 + \alpha_1 J)t}]$ . If  $N_1$  grows, the no. of fluorescing centers also increases, and supposing the luminosity of the discharge to be proportional to  $N_1$ , L. develops the empirical formula  $H = H_0(1 - e^{-kt})$ , where  $H_0$  is a const. and  $k$  is equal to  $(\alpha_2 + \alpha_1 J)$ . That law remains in force both for the non-damped and the damped discharge, provided the total amt. of supplied energy is equal for the given interval of time. (Talbot's law, as generalized by the author in *C. A.* 9, 3022.) The developed theory was proved exptly., inasmuch as the value of  $H/N_1$  was found to be const. and the values of  $N_1$  and  $H$  were found to be proportional to  $J$  for a stationary state of fluorescence and for low ionization. The values of  $k$  calcd. from the exptl. data were fairly const.

M. G. KORSUNSKY

**The effect of pressure and gas content on the action of vacuum-tube detectors.** H. A. BROWN AND C. T. KNIPP. *Phys. Rev.* 19, 278-80(1922).—Both the gas and pressure were varied in various types of detector tubes to det. the comparative audibility and intensity of response. It was found that (1) a pressure of 0.0025-0.05 mm. Hg gave 2-3 times as loud response as 0.05 mm.; (2) the operating voltage should be 40-50; (3) adjustment of voltage and current are easiest at the pressures above, and higher voltages than those in many low-vacuum tubes are advisable; (4)  $E_0 = e_1(a)^{1/2}$  where  $E_0$  = operating voltage,  $e_1$  = ionizing potential of the gas,  $P$  = pressure and  $a$  =

const.; (5) the bend in the curve of this equation occurs at the point of best audibility (0.003–0.005 mm.) and at voltages of 40–50, and with increasing pressure, adjustments of voltage and current become crit.; (6) Ne, N and CO<sub>2</sub> are no different from air in audibility or intensity of response, but A gives a louder and He and H a weaker audibility; (8) the degree of crit. adjustment of voltage and current for best response is approx. the same for air, N, Ne and CO<sub>2</sub>, but for H is more crit.; (9) the voltage is higher for He than for the others at the same vacuum; (10) the voltage is less crit. for He than for any other gas and is similar to a fair vacuum; (11) Hg vapor gives better response, has a lower voltage at similar pressures, and its voltage and current are less crit. than the other gases; (12) the audibility for all gases rises to a max. as the pressure is decreased below 0.005 mm.; and (13) the voltage at low vacuum depends on the ionization potential of the gas in the tube, but the former is 5–6 v. higher than the latter up to 0.06–0.08 mm. pressure.

C. C. DAVIS

**The excitation and ionization potentials of neon and argon.** G. HERTZ. *Proc. Acad. Sci. Amsterdam* 25, 442 (1923).—The values given in a previous communication (*C. A.* 17, 236) must be diminished by 0.7 v. on the basis of recent redets. of the abs. value of the standard first excitation potential of He.

E. D. WILLIAMSON

**The critical and dissociation potentials of hydrogen.** A. R. OLSON and GEO. GLOCKNER. *Proc. Nat. Acad. Sci.* 9, 122–5 (1923).—The dissociation potential of H<sub>2</sub> is definitely established as 3.16 v. Of the 8 breaks in the photoelec. current-potential curve, 5 are identified with the Lyman series, and the other 3 are ascribed to the H<sub>2</sub> mol.

G. L. CLARK

**The transmitted effect in selenium crystals.** J. C. POMEROY. *Phys. Rev.* 19, 414 (1922).—Using long needle-like crystals with electrodes clamped at one or more points measurements were made of the transverse cond. in the dark and also of the change in this cond. when a narrow band of light was allowed to fall at the electrodes and at points along the crystal. The log of cond. change is proportional to the distance between the electrodes and the spot of light. P. thinks that the light effect is transmitted along the crystal by some sort of wave motion.

W. F. MEGGERS

**The Zeeman effect.** E. BACK. *Ann. Physik* 70, 333–72 (1923).—The source of light was an arc in H at reduced pressure. The lines were photographed on a large grating in a magnetic field of about 35,000 gauss. Observations were made on Be, Th, Ba and Cu. The sepn. of the components, their intensities and the polarization are fully given. A fine line structure, not previously observed, is found in some lines outside of the magnetic field. The paper contains a large no. of tables giving the data together with detailed discussions of the structure and types of the various lines.

A. W. S.

**Secondary X-rays from crystals.** G. E. M. JAUNCEY. *Phys. Rev.* 19, 435–6 (1922); cf. *C. A.* 17, 679.—While the max. electrometer deflection for the Bragg spectrometer occurs when the angle of the ionization chamber is double that of the crystal, yet the deflection is appreciable at all other angles. The regularly reflected radiation is less than  $\frac{1}{2}$  of the total radiation emitted by the crystal at all angles up to 90°. At a crystal table angle of 7° and an ionization chamber angle of 60°, 46% of the primary beam is unabsorbed in Al, and 42.5% of the secondary, indicating some fluorescent radiation.

G. L. CLARK

**The beginning of the K and L series of X-rays.** F. L. MOHLER and P. D. FOOTS. *Phys. Rev.* 19, 434–5 (1922).—Measurements of the radiation from thermionic discharge in gaseous BCl<sub>3</sub>, CO<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>, CCl<sub>4</sub>, air, O<sub>2</sub>, Na, Mg, P, S and K were made by the photoelec. effect on electrodes within the same tube but carefully shielded from the discharge. The radiation current is a linear function of the voltage; hence changes in slope indicate crit. potentials. The K series limits of 4 elements in the first row of the periodic table are as follows: B, 66.4; C, 45.4; N, 33.0; and O, 25.8 Å. The L series limits of 5 elements in the 2nd row are: Na, 353, 725; Mg, 268, 374; P, 98, 112, 130; S, 81.2, 101; Cl, 62.5, 70.5, 78.6 Å. It is interesting to note that the ionization potential of He falls on the K line, and that of Ne on the principal L line.

G. L. CLARK

**Energy relations between X- and  $\beta$ -rays.** J. A. GRAY. *Phys. Rev.* 19, 430–1 (1922).—The relative amts. of energy between  $\beta$ -rays from Ra E and the X-rays formed when the former penetrate paper, Fe and Pb are connected by the expression  $E_2 = \lambda E_1 m$ , where  $E_1$  is the energy of the  $\beta$ -rays striking thin plates,  $E_2$  that of the X-rays,  $m$  the mass per unit area of the plates and  $\lambda$ , the mass transformation coeff., is 0.042 for C, 0.110 for Fe and 0.300 for Pb. The following percentages of  $\beta$ -ray energy are transformed: in paper, 0.4%; in Fe, 1.33%; in Pb, 6.0%.

G. L. CLARK

**Softening exhibited by secondary X-rays.** J. A. GRAY. *Trans. Roy. Soc. Canada* 16, III, 129–36 (1922).—See *C. A.* 16, 872.

G. L. CLARK

**The reflection by a crystal of X-rays characteristic of chemical elements in it.** GEO. L. CLARK AND WM. DUANE. *Proc. Nat. Acad. Sci.* 9, 126-30(1923).—As an additional procedure in a new method of analyzing crystal structures by X-rays (C. A. 16, 4134), the spectrum of the reflection from a given set of parallel planes is detd. by moving both crystal and ionization chamber, the latter at twice the rate of the former. For the 100 planes of KI a series of peaks, repeated in various orders, and characterized by a sharp absorption drop on the small angle side and by the greater intensity of the  $\beta$  than of the ill-defined  $\alpha$ -peak, is produced whenever the X-ray tube is operated above 33,000 v. (69,300 v. required for the characteristic line spectrum of W in the target). When the wave lengths producing the peaks are exptly. detd. by measuring the crit. voltages,  $V$ , in the quantum equation  $\lambda = hc/eV$ , where  $h$  is Planck's action const.,  $c$  the velocity of light, and  $e$  the charge of an electron, it is found that they are characteristic of I. These rays are excited in the crystal and reflected by the same crystal in accordance with the law  $n\lambda = 2d \sin \theta$ ; hence the spacing of planes containing I is obtained ( $d_{100}$  for KI =  $3.532 \times 10^{-8}$  cm.), which agrees with the value obtained with a wave length in the continuous spectrum. In the same way KI, gives the characteristic I spectrum, CsI and CsI<sub>2</sub> the Cs and I spectra, and CsIBr<sub>3</sub> the spectra of all 3 elements. By this means it has been possible to analyze monoclinic and orthorhombic crystals, and clearly to distinguish between Cs and I atoms in spite of the close similarity in reflecting powers.

G. L. CLARK

**The abnormal reflection of X-rays by crystals.** GEO. L. CLARK AND WM. DUANE. *Proc. Nat. Acad. Sci.* 9, 131-5(1923); cf. preceding abstr.—In addn. to the regularly reflected characteristic I spectrum from KI considered in the preceding abstract, these rays are also found to be reflected in an entirely anomalous fashion. The so-called X-peaks are found equidistant on either side of the 100 peaks at all ionization chamber angles between  $2^\circ$  and  $33^\circ$ , the position depending in a complicated fashion upon the angle of incidence. At  $2^\circ$  the angular sepn. from the 100 peak is  $19^\circ 38'$ ; at  $10^\circ$ ,  $17^\circ 38'$ ; at  $25^\circ$ ,  $10^\circ 22'$ ; and at  $30^\circ$ ,  $4^\circ$ . When the 100 planes are parallel to the incident beam the radiation enters the ionization chamber at  $23^\circ 36'$ . The wave length is const. for all angles and is characteristic of I. The X-peaks are produced at voltages above 33,000. No explanation of this anomalous reflection has been found.

G. L. C.

**The luminescence of solidifying antimony.** E. KARRER. *Phys. Rev.* 19, 437-8 (1922).—When Sb is heated to a temp. above its m. p. ( $630^\circ$ ) it becomes bright red. If it is then allowed to cool, its brightness will decrease with the temp. down to the point where solidification sets in, where a sudden increase in brightness occurs. The temp. also increases at this point. The phenomenon is, therefore, very similar to recalescence in iron. The brightness after the flash appears greater for a given temp. than the brightness at the same temp. before the flash. Thus it appears from this fact to be a case of crystal-luminescence. The phenomenon is not due to the oxidation of the Sb, since it takes place in H and in a vacuum. One sample of Bi showed the same phenomenon occurring at the same temperature. This was due to contamination of the Bi. Roughly one part of Sb in 2000 of Bi is sufficient to show luminescence.

W. F. MROGERS

**The spectrum of secondary X-rays.** A. H. COMPTON. *Phys. Rev.* 19, 267-8 (1922).—In order to obtain more definite information with regard to the characteristics of secondary X-radiation, a study has been made of the spectrum of the secondary rays excited in various substances by the X-rays from a Coolidge tube having a Mo target. A small piece of radiating material, such as celluloid or Al, placed in front of the first slit of the spectrometer, was illuminated by incident X-rays at approx.  $90^\circ$  with the secondary beam under investigation. The spectrum was studied by means of a calcite crystal grating, by both the ionization and photographic methods. The spectra obtained show lines identical in wave length with the primary K lines from Mo, thus proving that a part of the secondary radiation is truly scattered and unchanged in wave length. In addn. to these lines, a general radiation is observed which is more prominent in the secondary than in the primary beam. When the X-rays incident upon the radiator were unfiltered, the general secondary radiation had a broad intensity max. at a wave length slightly under  $1 \text{ \AA}$ . On introducing a Zr filter between the X-ray tube and the radiator, thus giving a primary beam consisting principally of the  $K\alpha$  line from Mo together with some fluorescent K rays from Zr, a much sharper max. in the secondary fluorescent radiation was observed. This result has been verified by means of photographic spectra, which show a max. of the general radiation at about  $0.95 \text{ \AA}$ , which is about 35% greater than the wave length of the exciting ray.

W. F. MROGERS

**New methods of crystal analysis and their bearing on pure and applied science.** WM. H. BRAGG. *J. Roy. Soc. Arts* 71, 267-77(1923).—This is a popular lecture devoted mostly to speculations on the structures of org. compds., upon which a few spectrum

observations have been made. After an outline of the structure of the diamond, graphite, naphthalene, anthracene, resorcinol, and tartaric acid are discussed from this point of view.

RALPH W. G. WYCKOFF

**Characteristic L absorption of X-rays for elements of atomic numbers 62 to 77.** J. M. CORK. *Phys. Rev.* 21, 326-33 (1923); cf. Hertz, *C. A.* 15, 1654.—C. photographed the 3 L absorption bands of Sa (62), Gd (64), Dy (66), Er (68), Yb (70), Ta (73), W (74), Os (76), Ir (77) together with the emission lines of W. The emission lines of W were used as reference lines in measuring the wave lengths of the absorption edges. The wave lengths and the frequency no. divided by the Rydberg const.,  $\nu/N$  values are tabulated. The energy levels within the atoms corresponding to the different absorption limits computed from the absorption and emission frequencies in terms of  $\nu/N$  are also given. The regular doublet differences  $\Delta(\nu/N) = (\nu L_2 - \nu L_1)/N = L_2 - L_1$  agree well with the values calcd. from the Sommerfeld formula. The empirical expression  $\Delta(\nu/N) = KZ^4$  approximates closely the observed values over the range of elements investigated.  $Z$  is the at. no. and  $K$  is a const. C. suggests a modified notation for X-ray emission lines.

L. M. HENDERSON

**The photochemical properties of the chromates.** J. S. PLOYNKOV. *Bull. acad. sci. Russ.* 1919, 1093-114.—P. attempts to clarify the question of the kinetics of photochem. reactions in chromates, with the following findings: (1) Neither  $\text{NH}_4$ , K nor Na chromate suffers any transformations if exposed to the most intensive sunlight in the absence of substances capable of oxidation. (2) In the presence of such substances both of the org. and inorg. type the photochem. reduction of the chromates and dichromates takes place rapidly even in the arc light. (3) The photochem. reduction results either in a brownish ppt. or a greenish soln., according to the properties of the substance which serves as an  $\text{O}_2$  absorber. (4) An evolution of a gas (either  $\text{NH}_3$  or  $\text{CO}_2$ ) is observed in some of the cases. ( $\text{NH}_3$  develops from  $\text{NH}_4$  chromates.) The quant. expts. were all carried out by using EtOH for the auxiliary substance, while both the chromates and dichromates were studied. The latter did not develop free  $\text{NH}_3$ , but were transformed by it into neutral chromates. The ppts. were too difficult to analyze to give a decisive picture of their compn. Theoretically the chromates should yield chromates, and the dichromates might transform both into chromic dichromates and chromates, though a no. of other compds. including bivalent and quadrivalent atoms of Cr can be expected. The expts. took place in a photo-thermostat, a uviolet lamp of 158 w. total load being used in connection with a screen, permitting 51% of blue rays of  $\lambda = 436\mu$  to enter the thermostat. The total time of each expt. amounted to 8 hrs., while 10.5 hr. and 12 hrs. expt. occurred occasionally. The kinetics of the primary reaction was as follows:

Table A. (Condensed by the abstractor.)

T°,	Init. concn. of chromate in milli-moles,	Init. concn. of alcohol in p. c.	Reaction const. × 100.	Max. deviation %
20	8.58 (bi)	87	36	3.0
20	8.45 (bi)	64	23	5
20	8.45 (bi)	48	16	6
20	8.71 (bi)	32	9.5	5
20	8.32 (bi)	8.1	4.8	One detn.
20	161.5 (bi)	64	40	10
20	25.1 (bi)	64	35	8
20	16.9 (bi)	30	30	3
20	8.45 (bi)	30	21	7
20	8.71 (mono)	87	39	2.5
20	8.45 (mono)	80	34	6
20	8.71 (mono)	64	24	8
20	328.45 (mono)	32	3.35	Two detns.
20	8.38 (mono)	8.1	3.1	One detn.
20	84.6 (mono)	64	53	5.5
20	48.0 (mono)	64	44	2
20	25.2 (mono)	64	29	7
20	17.0 (mono)	64	25	4
20	4.42 (mono)	64	9.6	8

The graphical interpretation of this table shows interesting anomalies, which cannot yet be explained. One of them is the linear run of the photochem. reduction even at the low concns. of chromates, while this should occur at such concns. only, as are



near the limit of light absorption. A series of expts. was undertaken to establish the temp. coeff., which proved to be very small—from 1.00 to 1.02 for each  $10^\circ$ . P. makes the hypothesis that this coeff. is common to all photochem. processes taking place in high-valency compds. of Cr, Mo, W, and U, while the figure 1.2 represents the coeff. for the photo-sensitive compds. of S, Se, Te, and the figure 1.4 for the halide compds. It was also shown that in the presence of EtOH the const. of light absorptions for chromate and dichromate solns. changes, and the color of the latter becomes deeper. The max. light absorption occurs at 23% alc. in chromate, and at 48% in dichromate solns.

M. G. KORSUNSKY

**Influence of low temperatures upon the light absorption factor of colored films.** P. P. LAZAREV. *Bull. acad. sci. Russ.* 1919, 169-74.—Two dyes, namely cyanine and pinacyanol, were tested so that a glass plate was covered either with a film of surface or substance dyed collodion, or by a continuous layer of the pure dye, obtained according to Pfüger's method. A Nernst lamp was used as a source of light and the plate was subject to its action both in plain air and in a liquid-air-cooled Dewar vessel. The absorption factor was detd. for the intervals of  $\lambda$  from 514 to  $680\mu$  for cyanine and 643 to  $644\mu$  for pinacyanol. The expts. have shown that, for the solid layer of dye, the temp. is of no influence. The cyanine-colored films acquire markedly different (lower) absorption factors for the extreme parts of the absorption bands at the lower temps. while the pinacyanol-colored exhibit a tendency to acquire a lowered absorption factor for the long waves, i. e., to have the absorption band broken up into two sep. bands. Six diagrams and tables, also a scheme of the app., are given.

M. G. KORSUNSKY

**Bromine addition to unsaturated hydrocarbons under the influence of light.** Part II, Chapter III-IX. I. S. PLOTNIKOV. *Bull. acad. sci. Russ.* 1916, 1563-94.—Chap. III deals with the continued development of equations related to the photochem. reactions taking place in systems with one or two photosensitive components, both in the light and the dark. Chap. IV deals with the application of the theory to the addition of bromine to the nitrile of the  $\alpha$ -phenylcinnamic acid. This reaction was investigated exptly. as described in Chapter V, where the numerical factors and equilibrium consts. are calculated for a const. light and the normal temp. In Chapter VI the relationship between the consts. and light intensity is proved to coincide with the results of theoretical calcs., and in Chapter VII the temp. factor is shown to be equal to 2.14 for  $10^\circ$  differences in the interval  $7-27^\circ$ . Chapter VIII shows the influence of the increased length of the way the rays of light have to pass within the photosensitive systems (by means of the total internal reflection) upon the equilibria, and discusses the methods of increasing the efficiency of photochemical process in the industry. The last chapter discusses the characteristic features of the consts. of velocities in photochemical reactions, which remain const. only in cases of absolute constancy of temp. light, concn., form and size of the space of reaction, etc. P. thinks that these consts. are in reality products of two variables,  $\alpha$  and  $\beta$ , of which the first represents the chem. resistance of the particular photosensitive system, or its chem. const., while the second is the const. of photochem. ionization. The exptl. investigations of P. proved also that bromine participates in the reaction not as  $\text{Br}_2$ , but rather as  $2\text{Br}$ . The equation of the equil. of the system studied was found to be  $Q = J/[1 - e^{-i\beta(b-y)}]^2$  ( $a - y)/\beta y$ .

M. G. KORSUNSKY

**The kinetics of photochemical reactions.** P. P. LAZAREV. *Bull. acad. sci. Russ.* 1919, 239-54.—A mathematical study of 3 types of photochem. reactions, the reversible, non-reversible and pseudo-reversible, under different conditions of light. Terms used:  $C$  = concn. of the photosensitive substance,  $J$  = intensity of light,  $k$  = absorption factor,  $\alpha_1$  = coeff. of reaction velocity,  $J_0$  = av. intensity of a periodically changing light,  $N$  = no. of periods in a unit of time,  $n$  = vibration no.,  $\alpha_2$  = velocity factor of the reverse reaction,  $J \times \varphi(C)$  = equation of the direct photo-reaction,  $\psi(C)$  = equation of the reverse reaction (taking place in darkness),  $t$  = variable time,  $T$  = definite interval of time,  $\alpha_3$  = factor of reaction velocity for the process of continuous supply of the photosensitive substance from an outside medium,  $A, B, D$  = integration consts.,  $x$  and  $d$  = the variable and the total thickness of the photosensitive layer,  $v$  = reaction velocity through the photosensitive layer,  $\beta$  = velocity factor of diffusion. The equations developed for the different cases of photochem. reactions are as follows: (1) For the general case of a non-reversible reaction taking place in const. monochromatic

light:  $\int_0^a dC/(1 - e^{-kC}) = \alpha_1 J t$ , a proof for the law of Bunsen-Roscoe; (1a) for the

special case of very small  $k$ 's or  $C$ 's:  $C_1 = C_0 e^{-\alpha_1 k J t}$ ; (1a<sub>1</sub>) same in a periodically changing monochromatic light:  $C_1 = C_0 e^{-\alpha_1 k J_0 t} \times e^{(1 - \cos 2\pi N t) \alpha_2 k J_0 / 2\pi N}$ ; (1a<sub>1</sub>') if  $N$

becomes very great, or the period of light intensity variations becomes very short, then:  $C_1 = C_0 e^{-\alpha_1 k J t}$  (this equation shows that the results of a const. and of a rapidly changing light of the same av. intensity are practically equal. Inasmuch as this theory was first expressed by Talbot for the reactions of the human vision, the author calls the last equation the formula of the Talbot law). (2a) For a non-reversible reaction in a mixed const. light limited by vibration numbers  $n_1$  and  $n_2$ , and if the photosensitive substance

possesses one band of absorption only, equation (1) remains, but  $J$  changes to  $\int_{n_1}^{n_2} J_n k_n n$ .

(2b) For the case of a substance absorbing two spectral bands or more and showing different reaction velocities in every one:  $dC/dt = [\alpha_1 \int_{n_1}^{n_2} J_n k_n n + \alpha_2 \int_{n_1}^{n_2} J_n k_n' n] \times C$ .

(2c) For a complex reaction, resulting in different products for the different bands of absorption, the calcn. must be simplified by substituting monochromatic light for the bands, and the process can be expressed by the equation:  $C_0 [1 - e^{-(\alpha_1 J_n k_n + \alpha_2 J_n k_n') t}] = C_1' + C_2'$ . (3a) For a reversible reaction in a const. light  $C_1' = [\alpha_1 k J C_0 / (\alpha_1 k J + \alpha_2)] [1 - e^{-(\alpha_1 k J + \alpha_2)(t-t_0)}]$ . (3b) For the same reaction in a periodically varying light:  $C_1' - C_2 = [\varphi(C)]' \times \int_0^{T_1} J dt - [\psi(C)]' T_1$ . (3b<sub>1</sub>) If a stationary

condition is reached, the equation becomes:  $[\varphi(C)]' \times \int_0^{T_1} J dt - [\psi(C)]' \times T_1 + [\psi(C)]' \times T_2 = 0$ . (3b<sub>2</sub>) For very small  $T_1$ , and no light during  $T_2$ , the equation is reduced to:  $\varphi(C) \int_0^T J dt = \psi(C) [T_1 + T_2]$ , or  $1/T \int_0^T J dt = \psi(C)/\varphi(C)$ .

(4) For pseudo-reversible reactions the general differential equations must be cor. by the addn. of members representing the removal of the reaction products and the supply of new photosensitive substance, both in light and in the dark. (5) If a non-sensitive substance of the concn.  $C_1$  takes part in the reaction by becoming ionized, the general differential equation of velocity becomes  $-dC/dt = \alpha_1 J_0 (1 - e^{-\alpha_2 C}) \times \varphi(C_1)$ , the  $\varphi(C_1)$  being of the exponential type. For small values of  $C_1$ , the  $\varphi(C_1)$  can be developed into  $[A_1 C_1 - A_2 C_1^2]$ . The reduced equation represents fairly well the photochem. oxidation of dyes, even when the member with  $C_1^2$  is eliminated. (6) For a reaction taking place through a layer of the thickness  $d$  with the products of the reaction being partly removed by diffusion the momentary concn. at a point in the distance  $x$  from the surface becomes  $C = A e^{-(\alpha_1 k J_0 - D_1 B_1) t/B x}$ .

M. G. KORSUNSKY

**Coincidence method for the wave-length measurement of absorption bands.** H. HARTRIDGE. *Proc. Roy. Soc. (London)* 102A, 575-587 (1923).—The method of coincidences has been applied to the direct visual measurement of absorption bands. In place of the ordinary cross wire of the spectroscope there is used an absorption band of the same width, mean density and distribution of absorption as that to be measured but reversed in direction. The absorption band used as an index and the absorption band to be studied have the same brightness and dispersion and each has passed through the pigment to be examd. The index spectrum may be shifted parallel to itself so that the two similar bands appear in line with the observer. To obtain two similar spectra lying side by side and reversed in direction, a reflection grating is used. By means of two prisms of small angle and a plane mirror light is incident on the grating from both sides of its normal. Two spectra are thus produced with their colors in reverse order. The prisms are chosen to have such angles that the spectra just lie side by side. They can be caused to shift with respect to each other by means of a micrometer mechanism, until there is coincidence of the absorption bands. The method of calibrating the micrometers for the spectroscope is described and exptl. values are given showing the accuracy. A method for the quant. estimation of pigments by the measurement of the wave length of their absorption bands is described. This estn. depends on the movement of the bands when the concn. of one pigment changes. As an example of the method, the estn. of the % satn. of blood with CO gas was made by a measurement of the wave length of the  $\alpha$ -absorption band. The accuracy of the measurement is about 0.6 Å. The probable error of setting two absorption bands into coincidence is but little greater than that of setting two sharp black lines into coincidence. A. W. SMITH

**The infra-red absorption of hydrogen chloride in the region 3.5 $\mu$  and at 200° K.** B. J. SPENCER AND C. HOLLEY. *J. Optical Soc. Am.* 7, 169-73 (1923).—The absorption

of HCl in the region  $3.5\mu$  was detd. at  $200^\circ\text{K}$ . and  $291^\circ\text{K}$ . The theory indicates a temp. variation of the envelope of the maxima of both branches of the curves for the near infra-red. The observations were made with a grating spectrometer, the receiving instrument being a specially constructed radiometer of the Nichols type. At room temp.,  $291^\circ\text{K}$ ., the maxima of the envelope of the fine absorption bands occur at  $3.419\mu$  and  $3.514\mu$ . There appears no shift of the wave lengths of the fine absorption bands as a function of the temp. This result is in accord with the theory. The position of the observed maxima of the envelope of the absorption bands at  $200^\circ\text{K}$ . and  $291^\circ\text{K}$ . is compared with the position of the maxima as calcd. from the theory of Kemble. At  $291^\circ\text{K}$ . there is fairly good agreement between expt. and theory. For  $200^\circ\text{K}$ . there is a divergence indicating that the theory may need modification at low temps. Because of the difficulty in locating the maxima of the envelope of the absorption bands, the deviation in the case of the low temp. may be due to the error in locating the maxima. In agreement with expt. the theory of Rieche gives the position of the bands of max. absorption for  $291^\circ\text{K}$ . as the third on each side of the center and for  $200^\circ\text{K}$ . as the second on each side of the center.

A. W. SMITH

Refraction in gases in the visible and infra-red ( $6.76\mu$ ) and determination of the characteristic vibration of calcite  $6.76\mu$ . MARTIN RUSCH. *Ann. Physik* 70, 373-90 (1923).—The wave length of the characteristic vibration of calcite at  $6.7\mu$  was detd. by an interferometer method, with a thermo-element as a detecting instrument. The center of gravity of this characteristic band was located at  $6763.2\mu\mu \pm 0.4$ . As the temp. of the "Reststrahlen" plates is increased the position of this center of gravity is slightly shifted toward larger wave lengths. This observation is only qual. The method of Loria and Patkowski was used for the measurement of the refraction in gases. This is an interferometer method in which is used the following formula, based on Gladstone and Dale's law for an ideal gas,  $n_0 - 1 = (n\lambda/L\Delta p) 760(1 + \alpha t)$ . Where  $n_0$  = the index of refraction,  $\lambda$  = the wave length,  $L$  = the double length of the gas cell,  $\Delta p$  = the change in pressure and  $n$  = the no. of displaced fringes. The observations which were made on air and A extend over the spectral region from  $546\mu\mu$  to  $6763\mu\mu$ . It is found that the dispersion curve given by Koch for air is in error in the infra-red. The formula of Helmholtz and Kettler  $n_0 - 1 = C/(n_0^2 - n^2)$  can represent the observed values with sufficient exactness only over a limited region of the spectrum.

A. W. S.

Centers of luminescence and variations of the gas pressure in spectrum tubes during electrical discharge. II. L. HAMBURGER. *Proc. Acad. Sci. Amsterdam* 25, 463-74; *Z. Elektrochem.* 29, 135-7, 142-4 (1923); cf. *C. A.* 17, 1374.—Polemic claiming priority and defending the views in earlier communications (cf. *C. A.* 15, 1459).

E. D. WILLIAMSON

Emission and absorption of halogens in the visible and ultra-violet regions. A. L. NARAYAN AND D. GUNNAYYA. *Phil. Mag.* 45, 827-30 (1923).—N. and G. have examd. exptly. the absorption and emission spectra of Cl, Br, and I vapors at different temps. and concns. The results are shown in a series of photographic reproductions of the spectrographs. The absorption spectra will be further examd. in the infra-red region.

S. C. L.

Absorption of potassium vapor. A. L. NARAYAN AND D. GUNNAYYA. *Phil. Mag.* 45, 831-4 (1923).—The absorption spectrum of K vapor has been detd. for the principal series lines for gradually increasing densities and for the greatest density at  $100^\circ$ . The red-channelled spectrum was detd. for 14 bands from 6811 to 6332.2 Å. Plates are given showing the photographic reproductions. Cf. *C. A.* 17, 365. S. C. L.

Wave-length measurements in the arc spectrum of gadolinium and dysprosium. C. C. KRESS. *Bur. of Standards, Sci. Papers* No. 466, 695-706 (1923).—The arc spectra of Gd and Dy were photographed from 5500 Å. in the green out into the infra-red. The materials used were  $\text{Gd}_2\text{O}_3$  and  $\text{Dy}_2(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$ , both of which were prepd. in a high degree of purity at the Univ. of Illinois. There were also available for measurement several spectrograms of Gd and Dy made by Eder of Vienna, of the materials prepd. by Auer von Welsbach. The wave-length tables contain about 950 lines for Gd and about 800 for Dy, most of which are faint. Among them are several having the appearance of band heads, indicating that each element emits faintly a banded spectrum.

C. C. KRESS

Spark spectra of higher orders. LÉON AND EUGÈNE BLOCH. *Compt. rend.* 176, 833-5 (1923).—A spark spectrum of the first order is one emitted by atoms which have lost one electron, those of higher order are emitted by atoms which have lost more than one electron. With an evacuated fused quartz tube contg. a drop of Hg, the electrodeless discharge was excited with a condensed discharge from a transformer, the tube being

heated in an elec. furnace. The disk of light emitted by the tube, when examd. spectroscopically, exhibited lines of two kinds: those extending entirely across the luminous area, and those extending only a short distance in from the edges where the elec. field is strongest. These two types of lines are analogous to the long and short lines of Lockyer. As the voltage of the discharge increases, the first type of lines decreases in intensity while the second type increases in intensity and tends to extend more across the luminous area. The first type of lines is regarded as spark lines of the first order, while the second type is of higher order. A brief wave-length table gives representative lines of each type.

C. C. KIESS

**A study of the luminous discharge in bromine.** A possible determination of the ionization potential of bromine. W. A. NOYES, JR. *J. Am. Chem. Soc.* 45, 1192-5 (1923); cf. *C. A.* 16, 3809; 17, 1376.—By a slight modification of the method described previously, the ionization potential of Br is found to be  $12.5 \pm 0.5$  v. About the same multiple of the ionization potential for a tube of given length is found as in the case of I. This is accounted for by the higher heat of dissociation of Br; its higher electron affinity would thus be counterbalanced by a lower concn. of the monatomic gas.

MARIE FARNSWORTH

**Intensities in the hydrogen spectrum.** A. L. L. HUGHES AND P. LOWE. *Phys. Rev.* 21, 292-300 (1923).—Variations of the intensity of H spectrum lines with the energy of the exciting electrons, 29 to 110 v., current and gas pressure being maintained const., was studied quant. by the use of a 3-electrode tube in which electrons from a long oxide-coated filament were accelerated through a nearby grid with a field-free space between the grid and the plate. The spectra of light from this space, excited with various accelerating potentials, were photographed on the same plate and the densities of certain lines were measured by a microphotometer. Of the series lines, H $\alpha$  shows practically const. density for the whole range of voltage, while H $\beta$ , H $\gamma$  and H $\delta$  increase in density at first rapidly and then more slowly, tending to const. values for higher electron energies. The density change was greater the higher the term no. Of the secondary spectrum  $\lambda\lambda 6327, 6225, 6135, 6122, 6030$ , and  $6018$  decrease very rapidly as the energy of electrons is increased, while  $\lambda\lambda 5013, 4934, 4929, 4743, 4632$ , and  $4205$  reach max. density between 30 and 40 v. and then grow weaker less rapidly than  $\lambda\lambda 6237$ , etc. Since the series spectrum is associated with the atom and the secondary with the mol., it is inferred that the ratio of dissociating to non-dissociating collisions increases rapidly with the energy of the electrons between 29 and 110 v. The change in relative intensity of the series lines suggests that the higher the energy of electron impact the more likely is the electron within the atom to be displaced to the remoter Bohr orbits when the mol. is dissociated.

K. BURNS

**The ultra-violet transmission of boiled absolute ethyl alcohol.** W. R. ORNDORFF, R. C. GIBBS AND M. SCOTT. *Phys. Rev.* 19, 393-4 (1922).—The transmission of boiled abs. alc. was measured and compared with that of freshly distd. abs. alc. For a layer 1 cm. thick the transmission of the boiled alc. was decidedly less than that of alc. which had not been heated after distn. from about  $0.37\mu$  to about  $0.24\mu$  (the shortest wave length studied). The max. decrease in ratio of transmission for 1-cm. layer was about 90%. The decrease in transmission increases with the time of boiling up to a certain point. Within small limits the change in transmission is the same for alc. boiled in flasks made of ordinary, Pyrex or Jena glass, or in a Ni-plated Cu flask. In all these cases the vapor produced by boiling was condensed and returned to the flask. The transmission increases slightly for a few days after the alc. is boiled. The alc. condensed from the vapor produced by boiling gave the same transmission as the un-boiled alc. It is quite possible that the change in transmission here described is due not to any real change in absorption but to a scattering produced by colloidal particles of the material of the flask or to oxidation of the alc.

W. F. MEGGERS

**Arc, spark and absorption spectra of argon.** W. W. SHAVER. *Trans. Roy. Soc. Canada* 16, III, 135-44 (1922).—With a simple lamp of the 3-electrode type contg. pure Ar at 0.1 mm. Hg pressure, the radiation produced by electron bombardment with an applied potential of 10.1 v. was detected spectrographically. With accelerating fields from 16 to 30 v. only lines of the so-called red spectrum of Ar appeared but at 31 v. the blue spectrum, assumed to be enhanced, began to appear. An attempt was made to produce a third type of spectrum by use of a potential of 240 v. but no new lines appeared. Various attempts to detect an absorption spectrum of Ar, between the wave length limits 7000 and 2150 Å., were unsuccessful. Both ionized gas at pressures of 2, 5 or 155 mm., and Ar at an equiv. pressure of 102.4 atms. were found to be transparent between the wave lengths mentioned.

W. F. MEGGERS

Two new lines in the aluminium spectrum and their possible series relations.

G. D. SHALLENBERGER. *Phys. Rev.* 19, 398-9(1922).—A high-potential elec. spark between Al electrodes shows two lines,  $\lambda$  4150.6 and 2907.4, hitherto unidentified, but now ascribed to Al. Their series relations are suggested but the evidence is not convincing.

W. F. MEGGERS  
The spectrum of helium in the ultra-violet. W. GROTRIAN. *Naturwissenschaften* 11, 321-3(1923).—A discussion of the work of Lyman (cf. C. A. 16, 3589) and Franck (cf. C. A. 17, 489).

C. C. DAVIS  
The 3872 band of the Swan spectrum; its modification in a magnetic field. M. R. FORTRAT. *Ann. phys.* 19, 81-92(1923).—F. previously described magnetic modifications of some spectral bands (*Ann. phys.* 3, 282(1915)) and announced a simplification of certain doublets and triplets forming regular sequences. The general character of this effect was the absence of polarization and a contraction of a group of rays, with const. ratio  $ndn/H^2$ , where  $n$  represents the sepn. of the normal doublet and  $dn$  its contraction in the field  $H$ . This ratio was called the sensibility of the group. Precise measurements on the 3883 band of  $N_2$  by Bachem confirmed these results with two modifications, the sensibility ratio  $\sigma = ndn/[H^2(1 - (dn/n))]$ , and this varies from one doublet to another, decreasing as the order no. increases. The  $\lambda$  5872 complex of the Swan spectrum comprises two bands; the one most important because of its range and intensity consists of 2 sequences of doublets, the other consisting of 3 sequences, 1 of doublets and 2 of single lines. A table of wave nos. is given for all these lines. Modifications of this band were studied in fields from 4300 to 34600 gauss, observations being made in a direction perpendicular to the lines of force and values of  $\sigma$  are given for the 2 polarizations—parallel and perpendicular to the lines of force. Qualitatively, the lines of the same sequence show the same magneto-optic effects. The single lines are doubled in each polarization but the doublet sepn. does not appear to obey a simple law. The magnetic modification of double lines indicates that they would become single lines in intense fields but too little is known about the normal Zeeman effect in bands to decide if there is an effect for bands analogous to the Paschen-Back effect in spectral series.

W. F. MEGGERS  
The vacuum spark spectrum of silicon. R. A. SAWYER AND R. F. PATON. *Phys. Rev.* 19, 256-7(1922).—Wave-length measurements on Si by various observers are not in satisfactory agreement. A new list of 55 lines between 4085.25 and 6372.2 Å. is obtained from prism spectrograms of a Si spark *in vacuo*. The wave lengths may be 0.1-0.3 Å. in error. Nineteen pairs of lines suspected of having const. sepn. are tabulated. These wave-no. differences cluster about 61, 17 and 34.

W. F. MEGGERS  
Further experiments on critical potentials in hydrogen. F. L. MOHLER, P. D. FOOTE AND E. H. KURTH. *Phys. Rev.* 19, 414-5(1922).—The discrepancies between previous results of various observers as well as the differences in interpretation of results led to the following expts. A 4-electrode tube was constructed with a photoelec. source of electrons instead of the usual thermionic cathode. A KH surface illuminated by an incandescent lamp gave currents ample for measurement of the crit. potentials. The ionization potential was found to be 16.0 v. and inelastic impacts occurred at 10.5 and 22.3 v. When a Wehnelt cathode replaced the photoelec. one the results were practically identical with the above at the same pressures. With higher pressures inelastic impacts occurred at 10.5, 16 and 21 v. It is concluded that the dissociation of  $H_2$  by an incandescent wire plays no appreciable part in the phenomena observed. The potentials of inelastic collision at 10.5 and 22.3 indicate resonance potentials at 10.5 and 11.8 v., due to collisions with normal H. The possibility that 22.3 v. is a resonance potential and not due to successive impacts is not excluded by this work.

W. F. MEGGERS  
The aspherical nucleus theory applied to the principal series of helium. LUDWIG SILBERSTEIN. *Phys. Rev.* 19, 399(1922).—The quantum theory of spectral emission combined with the assumption of a non-spherical, axially symmetrical nucleus is applied to Fowler's principal series of He. The coeff. of asphericity is detd. to be  $9.334 \times 10^{-4}$ , and the modified Rydberg const.  $N = 109723.22$ . The latter combined with a previously obtained value of  $N$  for H gives the ratio of the mass of the H atom to that of the electron the value 1817.

W. F. MEGGERS  
The infra-red absorption spectra of diatomic gases and their ionization potentials. E. C. KEMBLE. *Phys. Rev.* 19, 394-5(1922).—The Lenz theory of the infra-red band spectra of gases is simply an application to mol. rotational and vibrational motion of the Wilson-Sommerfeld quantum conditions, the Bohr frequency principle and the principle of selection. Using a method of integration in series to evaluate the quantum integral, K. obtains a new formula for the frequencies in the infra-red absorption of a diatomic gas. The formula is in rough agreement with certain exptl. relations between

the coeffs. of the vibrational quantum no. and is further tested by calcn. of ionization potentials. For HCl the ionizing potential is 14 v., while for HBr a rough calcn. yields  $12 + v$ .

W. F. MCGEE

**Change of conductivity of phosphorescent substances in the emission of light by heat.** E. RUPP. *Ann. Physik* 70, 391-404(1923).—The expts. of Lenard and Sacland and Gudden and Pohl show that there is a change in the cond. of phosphorescent substances when acted on by light. In some cases there is a change of cond. when the substance is exposed to infra-red rays. In these expts. the change in cond. of the phosphorescent substances is studied when the substance is caused to emit thermo-phosphorescence. The dependence of this change on the applied elec. field and on the nature of the emitted light was investigated. In all cases an increase of cond. is found. It is proportional to the total light emitted by the phosphorescent substance and for a particular substance the total emission of light in abs. measure is independent of the position of the spectral band. The change of cond. increased with the temp. For small elec. field the quantity of electricity is nearly proportional to the applied field. For large values the curve showing the relation between the field and the quantity of electricity becomes parallel to the axis of elec. field. The change of cond. is independent of the thickness of the layer. It is caused by the fact that the returning electrons which have been freed by the heat, produce a number of secondary electrons to carry the elec. current. The observed proportionality between the change of cond. and the total quantity of light is made the basis of a method of measuring the quantity of light.

A. W. S.

**The reduction of carbon dioxide by ultra-violet light.** H. A. SPOHR. *J. Am. Chem. Soc.* 45, 1184-7(1923).—A repetition of the expts. of Usher and Priestley (*C. A.* 5, 3466), Berthelot and Gaudechon (*C. A.* 4, 2480), Stoklasa (*C. A.* 6, 501), and Baly (*C. A.* 15, 3072), upon the reduction of  $\text{CO}_2$  by ultra-violet light failed to give a definite test for  $\text{CH}_2\text{O}$  in any case. It is concluded that in those investigations where such a reduction has been reported, essential conditions must have existed which were not described in the publications, or else that there has been some misinterpretation of exptl. observations.

A. P. LOCKE

Recent determinations of the susceptibilities of oxygen and nitric oxide and the magneton (PERRIN) 2. Chemical action of light (Scagliarini, Saladini) 10. Photosensitiveness of some urethans (Korczynski, Grzybowski) 10.

PERRIN, JEAN: *Atoms*. 2nd English Ed. Revised. Authorized translation from 11th revised French edition by D. L. Hammick. London: Constable & Co., Ltd., 231 pp. 8s. 6d. Reviewed in *Chem. News* 126, 271(1923).

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

**Electric furnace practice.** J. PERRIN. *J. four elec.* 32, 48-50(1923).—A review. Cf. *C. A.* 17, 1924.

C. G. F.

**Design and construction of electric furnaces.** L. J. BARTON. *Blast Furnace & Steel Plant* 11, 272-6(1923).—A review.

C. G. F.

**Industrial electric heat applications.** J. L. MCK. YARDLEY. *Elec. World* 81, 987-9(1923).—A review.

C. G. F.

**Martin and electric steel works of reinforced concrete.** JULIUS MAGG. *Z. Ver. deut. Ing.* 67, 405-7(1923).

E. J. C.

**Manufacture and application of carbon electrodes.** FRANCOIS GAILL. *J. four elec.* 32, 60(1923).—Description of the process as practiced at the Notre Dame de Briançon works.

C. G. F.

**The electrolytic extraction of copper by the Greenawalt process.** "P. B." *Genie civil* 82, 85(1923); cf. *C. A.* 16, 1049.—Presence of Fe in the electrolytic bath is very objectionable. During electrolysis ferric Fe is produced at anode and recombines with the Cu deposit at the cathode, giving ferrous Fe, which reduces the yield of Cu.  $\frac{1}{4}\%$  of  $\text{Fe}(\text{SO}_4)_3$  is enough to destroy the practical value of the process. The G. process consists in reducing ferric salts by  $\text{SO}_2$ , by CuS and by combination of the two, in reducing chambers. Reduction is more complete in these reducing chambers than in towers and higher temp. may be used. The CuS is pptd. in very dil. and very impure solns. and the CuS has its own value as a reducing agent.

JACK J. HINMAN, JR.

The action of colloidal gelatin on electrolytic cadmium. E. MILLIAU. *Bull. soc. chim. Belg.* 32, 143(1923).—Grube and Ruess (*C. A.* 15, 1463) have found that by adding gelatin to a  $\text{CuSO}_4$  soln. the electrolytic Cu deposit will be much smoother and compact. M. shows that the same holds true for an electrolytic Cd deposit from  $\text{CdSO}_4$ .

R. BRUTNER

Electrolytic preparation of alkali permanganate by anodic dissolution of manganese by means of a superimposed alternating current. G. GRUBE and H. MEYER. *Z. Elektrochem.* 29, 100-5(1923); cf. *C. A.* 17, 1371.—Direct-current electrolysis of a soln. of  $\text{K}_2\text{CO}_3$  with a Mn anode, gives very poor current yields (25-30%) of  $\text{KMnO}_4$  at room temp. The yields are but slightly increased by superimposing an a. c. Although an increase occurs with medium a. c. densities, at higher densities the yield falls below that obtained with d. c. alone. The favorable action of the superimposed a. c. is due to the fact that it diminishes the decrease in alkali about the anode. At higher a. c. densities the decrease in the yield depends upon the depolarizing action of the a. c., thus promoting the formation of manganate.

H. JERMAIN CREIGHTON

Electrochemistry of non-aqueous solutions. III. Electrodeposition of alkali metals from solutions in water-free pyridine. R. MÜLLER, F. HÖLLZ, A. PONTONI and O. WINTERSTEINER. *Monatsh.* 43, 419-37(1923); cf. *C. A.* 17, 1386.—Conditions attending the electrolytic sepn. of Li from  $\text{LiCl}$  and  $\text{LiNO}_3$ , Na from  $\text{NaI}$ ,  $\text{NaNO}_3$  and  $\text{NaSCN}$ , and K from  $\text{KSCN}$ , all in water-free pyridine soln., have been studied. A Hg cathode and a Pt anode were used. Electrolysis was carried out with various c. ds. up to 0.2 amp./dm.<sup>2</sup> Measurements were made of (1) the anodic and (2) the cathodic deposition potential, (3) the cathodic polarization after interrupting the current, (4) the sum of the single potentials of the anode and cathode, (5) the decompn. potential and (6) the e. m. f. of chains of the type  $\text{M}[\text{MX}]/\text{Ag-pyridine-electrode}$ . The presence of 5 and 10%  $\text{H}_2\text{O}$  in the pyridine gives results wholly different from those obtained with anhyd. pyridine, probably owing to the sepn. of alkali hydroxide.

H. J. C.

Electrolysis of acetic acid with a commutated direct current. E. BAUR. *Z. Elektrochem.* 29, 105-10(1923).—Solns. of  $\text{AcOK}$  in  $\text{AcOH}$  when electrolyzed at high c. ds. with a commutated d. c. of low frequency, decompose with the formation of  $\text{H}_2$ ,  $\text{CO}_2$  and a mixt. of hydrocarbons consisting mostly of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . These products are formed in accordance with the following equations: (1)  $2 \oplus + 2\text{CH}_3\text{CO}_2^- = \text{CH}_3\text{CO}_2\text{CO}_2\text{CH}_3$ ,  $2 \ominus + 2\text{H}^+ = 2\text{H}_2$ ,  $\text{CH}_3\text{CO}_2\text{CO}_2\text{CH}_3 + 2\text{H}_2 = 2\text{CH}_4 + 2\text{CO}_2$ ; (2)  $2 \oplus + 2\text{CH}_3\text{CO}_2^- = \text{CH}_3\text{CO}_2\text{CO}_2\text{CH}_3 = \text{C}_2\text{H}_6 + 2\text{CO}_2$ .

H. J. CREIGHTON

Electrochemical preparation of tin hydride. F. PANETH. *Z. Elektrochem.* 29, 97-8(1923); cf. *C. A.* 14, 1494; 15, 1456.—Previous methods employed for the prepn. of Sn hydride are reviewed. It has not been possible to prepare this compd. either by Ernyei's electrochem. method for the prepn. of  $\text{TeH}_2$  (cf. *Z. anorg. Chem.* 25, 313(1900)) or by P.'s method for the prepn. of  $\text{SbH}_3$  (cf. *C. A.* 15, 213). The gas has been prepd., however, by electrolyzing a dil.  $\text{H}_2\text{SO}_4$  soln. of Sn, using a Pb cathode and a diaphragm. The cathode gases on being condensed with liquid air yielded a liquid contg. 10% Sn hydride.

H. JERMAIN CREIGHTON

Electrodeposition of bronze. GIUSEPPE ONGARO. *Met. ital.* 15, 63-6(1923).—Very good results are obtained by adding to the electrolytic bath small quantities of a substance contg. the constituents of dicyanodiamide, oxalic acid and  $\text{PhNHNH}_2$ . The substance is thought to be a mixt. of  $\text{NH}_4$  oxalate and phenylguanazole. It is prepd. as follows: Boil 450 g. Ca cyanamide (18-20% N) with  $\text{H}_2\text{O}$  and pass a current of  $\text{CO}_2$  through the mixt. Boil again and filter. Conc. by heat, add 90 g. oxalic acid dissolved in 50 cc. boiling  $\text{H}_2\text{O}$  and 205 g.  $\text{PhNHNH}_2$ . On cooling the liquid becomes a cryst. mass. The efficiency of the above substance in the deposition of bronze depends on the presence of (1) the  $(\text{PhNNH})$  group, which shows reducing properties superior to any other org. compd.; (2) the oxalic group, which is the best agent for obtaining an elastic, compact, adherent cathode deposit; and (3) the amide group.

ROBERT S. POSMONTIER

Silver-plating apparatus for the chemical industry. O. HAHN. *Chem. App.* 10, 53-4(1923).—General remarks, with a cut of an app. for showing the amt. of Ag deposited.

J. H. MOORE

Anodic oxidation of gold. F. JIRSA and OT. BURVÁNEK. *Z. Elektrochem.* 29, 126-35(1923); cf. *C. A.* 17, 1578 and following abstr.—The anodic oxidation of Au in  $\text{H}_2\text{SO}_4$  takes place step-wise, and may be represented as follows: 1st. stage (active)  $\text{Au} \rightarrow \text{Au}^+$ ; 2nd. stage (passive)  $3\text{Au}^+ \rightarrow 2\text{Au} + \text{Au}^{+++}$ ; 3rd. stage (active)  $\text{Au} \rightarrow \text{Au}^{+++}$ ; 4th. stage (passive)  $\text{Au}^{+++} \rightarrow \text{Au}^{++++} \rightarrow \text{Au}^{++}$ . The fact that bivalent Au ions are not formed at Au anodes, i. e.,  $\text{Au} \rightarrow \text{Au}^{++}$  and  $\text{Au}^+ \rightarrow \text{Au}^{++}$ , is attributed to hydrolysis of  $\text{Au}_2\text{SO}_4$ .

H. JERMAIN CREIGHTON

**Anodic oxidation of gold.** FR. JIRSA AND OT. BURYÁNEK. *Chem. Listy* 16, 299-305(1922); cf. C. A. 17, 1578 and preceding abstr.—A strong current was passed through a cell having a gold anode, and dil.  $\text{H}_2\text{SO}_4$  as electrolyte. After 24 hours the current was stopped, and the back e. m. f. of the anode measured. For the cell  $\text{Au}|\text{Au}_2\text{O}_3\cdot\text{NH}_4\text{SO}_4|\text{NH}_4\text{SO}_4\cdot\text{H}_2\text{O}|\text{Pt}$  this was +1.24 v. at 18°. The same voltage was obtained whether the anode was prepd. in the dark, or in the light of a mercury-vapor lamp, and reduction of the strength of acid from normal to 0.001 *N* made no difference in this result. The rates of polarization of gold anodes, currents of 0.02 and of 0.5 milliamperes/sq. cm. being used, were next measured, and the results shown on a graph. Below 0.02 milliamperes, the results were untrustworthy, owing to the slow rate of oxidation producing passivity in the gold. The rate of discharge of polarized gold anodes was measured, under various conditions, and with the introduction of different resistances, in order to retard the rapidity of discharge. Gold anodes were next depolarized by passing currents of increasing magnitude through the cathode, until the polarization e. m. f. disappears. The magnitudes of the polarization currents produced by stationary and rotating oxidized gold anodes, different concns. being used, were measured, and curves drawn showing the relation between the galvanometer readings and the voltage.

J. C. S.

**Variation of the electromotive force of a Weston cell (in quartz) under the action of ultra-violet light.** J. POUONER. *Rev. gén. élec.* 12, 514-6(1922); *Science Abstracts* 26A, 95.—Ultra-violet light from a Cooper-Hewitt lamp was used. The e. m. f. was always above that of a similar cell in glass. An equation of correction of the voltage for change of temp. of the cell is given and extended tables of temp., times of exposure to ultra-violet light, and resultant e. m. f.'s. P. shows the results are not due to mere variation of temp. of the cell, as this for the Weston cell is of the order of 1 in 10,000, while the results obtained are of the order 1 in 100. The various chem. reactions which occur in the cell are discussed. P. has noticed a greater change in the  $\text{Hg}_2\text{SO}_4$  on the side of the cell exposed to the rays, a result which has been confirmed by expts. on  $\text{Hg}_2\text{SO}_4$  itself, which undergoes a reversible change to Hg and  $\text{HgSO}_4$ .

H. G.

**Electric purification of gases and fumes.** E. M. ISAAC. *Bull. soc. fed. ind. chim. Belg.* 2, 239-52(1923)—A review.

R. BEUTNER

**Alternating-current projection lamp with high intrinsic brilliancy.** B. SCHÄFER. *Elektrotechn. Z.* 44, 335-6(1923).—By using one horizontal light carbon and 2 vertical auxiliary carbons which conduct current of displaced phase, S. obtains a single-phase projection lamp with higher intrinsic brilliancy and less flicker than the ordinary 2-carbon lamp.

D. MACRAE

Oscillations of temperature of an incandescent filament and the specific heat of tungsten (SMITH, BIGLER) 2. Graphs for calculation of electron emission from tungsten, etc. (DUSHMAN, EWALD) 2. Solidification diagram for the system  $\text{MgCl}_2\text{-KCl-BaCl}_2$  (MATIGNON, VALENTIN) 2.

**Storage battery.** W. H. THORPE. U. S. 1,454,571, May 8. Structural features.

**Storage battery.** H. G. WAGNER. Can. 230,528, Apr. 24, 1923. The positive and negative elements are made of porous material and accumulator active material and have voids therein for contg. electrolyte.

**Electrolyte for storage batteries.** L. E. BROWNELL. Can. 230,781, May 1, 1923. A battery filling compd. consists of  $\text{H}_2\text{SO}_4$  and water (dilin. not specified) 0.8 gals.  $\text{MgSO}_4$  0.5 alum 0.25 and glycerol 0.33 lbs.

**Storage-battery electrolyte.** E. J. RUEB. U. S. 1,454,078, May 8. Al K sulfate is used, with  $\text{H}_2\text{O}$  (1 of alum to 8 of  $\text{H}_2\text{O}$ ) in order to replace  $\text{H}_2\text{SO}_4$  soln.

**Positive elements for storage batteries.** H. G. WAGNER. Can. 230,527, Apr. 24, 1923. Wood is treated with a soln. of  $(\text{NH}_4)_2\text{SO}_4$  then covered with accumulator oxide and the latter covered with C, the C is covered with  $\text{CaSO}_4$  and the whole is dried or otherwise treated to create voids in the material.

**Storage-battery containers.** A. BUGBEE. Can. 230,129, Apr. 10, 1923. A container for storage batteries is formed of an integral piece of hard porcelain and is divided by partitions formed integral with the container into several cell chambers.

**Storage-battery grid.** A. O. CARRETT, C. E. FUNNELL and W. L. HOFFMAN. Can. 230,109, Apr. 10, 1923.

**Electric battery.** D. PEPPER. U. S. 1,454,943, May 15. The battery comprises an outer Pb cup with active material such as  $\text{PbO}_2$  in close contact with the inside of the cup constituting the cathode of the battery, an inverted Zn cup within and spaced



from the active material layer, a seal at the top of the battery between the Zn and Pb cups, and an electrolyte, e. g., dil.  $\text{H}_2\text{SO}_4$ , in contact with both electrodes.

**Iron and steel.** W. E. F. BRADLEY. Can. 230,926, May 8, 1923. A hydrocarbon gas is passed through the molten ore in an elec. furnace. The continuous supply of ore to the furnace is interrupted at intervals for discharging the reduced product.

**Electric furnace for producing iron and steel.** W. E. F. BRADLEY. Can. 230,924, May 8, 1923. An elec. furnace has a carbon tuyère independent of the electrodes and so disposed as to be covered by the charge in one position of the furnace and removed therefrom in another and means for supplying reducing gas to the tuyère. Cf. C. A. 16, 3596.

**Electrolytic reduction of lead sulfate.** F. N. FLYNN and G. D. VAN ARSDALE. U. S. 1,448,923, Mar. 20.  $\text{PbSO}_4$  is dissolved in a nearly satd. brine or soln. of  $\text{NaCl}$ ,  $\text{BaCl}_2$  or  $\text{CaCl}_2$  contg.  $\text{FeCl}_2$  or other easily oxidizable salt. This soln. is electrolyzed with a Pb or Fe cathode and an insol. anode which may be formed of graphite, C, magnetite or an insol. Fe-Si alloy. Ferric salts resulting from the depolarizing action of the  $\text{FeCl}_2$  during the electrolysis are reduced by  $\text{SO}_2$  or other suitable reducing agent. Lime is added to ppt.  $\text{SO}_4$  as  $\text{CaSO}_4$  and after removal of the ppt. the soln. may be reused for dissolving fresh quantities of  $\text{PbSO}_4$  for electrolysis.

**Electric production of sulfides.** R. RODRIAN. Can. 230,269, Apr. 10, 1923. An elec. current is passed through a soln. of a hydroxide of an alkali or alk. earth in contact with comminuted S until a sulfide is formed. If a sulfide of a heavy metal such as Pb is desired, finely divided Pb is also placed in contact with the electrolyte.

**Lead powder.** JYUGI OHSHIMA and the FURUKAWA DENKI KOGYO KABUSHIKI KAISHA. Japan. 41,177, Dec. 19, 1921. A 0.1-3% soln. of Pb benzene- or naphthalene-sulfonate is electrolyzed with metallic Pb electrodes, at 2-5 v. and 0.1-5 amp. After drying the deposit is easily pulverized;  $\text{PbO}_2$  and  $\text{Pb(OH)}_2$  are not included.

**Apparatus for electric precipitation of suspended particles from gases.** H. A. WINTERMUTE. U. S. 1,454,256, May 8. A flexible discharge electrode is arranged so that it may be swung into contact with the collecting electrode to clean the electrode.

**Apparatus for electric precipitation of suspended particles from gases.** C. H. WEISKOPF. U. S. 1,454,255, May 8.

**Electric heating of metals.** A. E. GREENE and W. B. RUNYAN. U. S. 1,455,747, May 15. In treating Fe or other metals in an elec. furnace, a secondary circuit of molten metal is formed around a magnetic core, current is induced in the secondary circuit by means of the core and the metal is caused to flow continuously into the circuit and out at a different point after being heated.

**Electric furnace.** W. E. F. BRADLEY and A. B. BRADLEY. Can. 230,927, May 8, 1923. The furnace has its main axis inclined and has a door and a tuyère both removed from the main axis and means for rotatably supporting the furnace. The symmetrically arranged electrodes terminate above the charge, are inclined toward a common axis and have individual feed devices controlled by the current passing through the respective electrodes for maintaining their ends at equal distances from the common axis.

**Electric induction furnace.** A. E. GREENE. U. S. 1,455,748, May 15.

**Electric furnace flue closures.** W. E. F. BRADLEY. Can. 230,929, Mar. 8, 1923. An elec. furnace has a C roof, means for maintaining a reducing atm. within the furnace during the removal of the charge and means for automatically closing the charging flue.

**Electrically heated salt-bath furnace.** O. A. COLBY. U. S. 1,454,847, May 15. The furnace is adapted for tempering steel tools.

**Carbon electrode for furnace.** HITOSHI ISHIKAWA and THE NIPPON CARRON KABUSHIKI KAISHA. Japan. 41,187, Dec. 19, 1921. The electrode is a C tube closed at one end. It is of uniform compn., light, and distributes elec. current homogeneously.

**Electroplating with cadmium.** WM. A. WISSLER and C. H. HUMPHRIES. Can. 230,277, Apr. 10, 1923. Fe or steel articles are made rust-proof by coating with Cd by passing a current of high density through a basic or neutral cyanide soln. of Cd from a graphite, C or non-polarizing anode. The coated article is then baked at 150-250°.

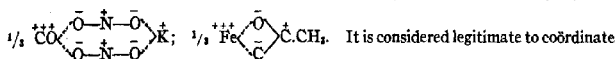
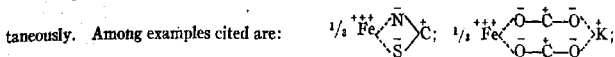
## 6-INORGANIC CHEMISTRY

H. I. SCHLESINGER

**Factors influencing coördination.** T. M. LOWRY. *Chemistry & Industry* 42, 316-9(1923).—The fundamental factor is close-packing of ions as in crystals. As in these, negative ions can link together ions of metal but 2 metal ions can share only 3 negative ions as only 3 apices in 2 adjacent octahedra can be brought together. In

the case of bivalent anions contg. O the bridges between O atoms reduce the symmetry to a point where optical activity becomes possible even in simple compds. like  $K_4[Fe(C_2O_4)_4]$ . The completion of shells of electrons is a factor in detg. stability of co-ordinated compds. In compds. of  $Fe^{II}$ ,  $Co^{III}$ ,  $Rh^{III}$ ,  $Ir^{III}$ ,  $Pd^{IV}$  and  $Pt^{IV}$ , 6 groups are just sufficient to complete the outer shell of the metal atom if each group shares one pair of electrons with the metal. Hence the stability of the hexammines of these metals and carbonyls such as  $Mo(CO)_6$ ,  $Fe(CO)_5$  and  $Ni(CO)_4$ . While a deficiency of 1, 2 or 3 electrons is tolerated readily, the surplus electron of  $K_4[Co(CN)_6]$  is violently expelled to form the very stable cobalticyanide. The shortage of one electron in  $Fe^{II}$  in  $K_4[Fe(CN)_6]$  permits considerably more stability. Tautomeric ions, which can be written in two ways since they possess 2 possible points of attachment for H or alkyl, often form complexes in which the multivalent metal ion is attracted to both points simul-

taneously. Among examples cited are:



It is considered legitimate to coördinate the univalent metal with 2 negatively charged O atoms when in the undissociated state or in a crystal; but this must be regarded as the very weakest type of coördination.

A. R. MIDDLETON

**Constitution of hydrates. I. Systematization of the hydrates of salt-like compounds.** M. E. LEMBERT. *Z. physik. Chem.* 104, 101-46(1923).—Spatial nos. are deduced on the basis of simple geometric conceptions of coördinate union, such as the Werner-Kossel hypothesis, which represent the possible coördinations nos. for similar adds. to a central atom. By means of these spatial nos. the solid hydrates of salts can be systematized. The simultaneous effect of the ions in the formation of hydrates is discussed, and Fajan's hypothesis (cf. *Naturwissenschaften* 9, 729) is confirmed. The system has been tested successfully with metal chlorides, sulfates, nitrates and hydroxides.

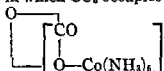
H. JERMAIN CREIGHTON

**Boron hydrides. VI. The simplest hydrides.** ALFRED STOCK AND ERNST KUSS. *Ber.* 56B, 789-808(1923).—The earlier work was repeated under improved conditions resulting from (1) fuller knowledge of Si hydrides which are always in the gas mixt., (2) the vacuum app., (3) employment of fractional condensation instead of fractional distn. for purification, (4) tension-thermometric measurement of low temps. The new material is presented in highly condensed form in the following divisions: (1) Analytical detn. of Bi. (2) Prepn. of Mg boride; Mg could not be obtained with Si lower than 0.1%,  $B_2O_3$  of less than 0.01% Si. (3) Decompn. of Mg boride by HCl (sketch of improved app.). (4) Preliminary sepn. of the crude condensate (6-7 cc. liquid from 2 kg. of boride); temp. of distn. vessel raised in 7-8 hrs. from  $-150^\circ$  to  $-30^\circ$  (5 hrs.  $-100^\circ$  to  $-80^\circ$ ); fraction in order of amts., distn. vessel  $-30^\circ$ ,  $B_4H_{10}$ ,  $B_{10}H_{14}$  and higher Si hydrides; (I)  $-60^\circ$ ,  $B_4H_{10}$  and  $SiH_{10}$ ; (II)  $-95^\circ$ ,  $B_4H_{10}$ ,  $Si_2H_6$  and a little  $B_4H_{10}$ ; (III)  $-120^\circ$ ,  $B_4H_{10}$ , some  $Si_2H_6$  and  $Si_2H_8$ , traces of  $H_2S$ ; (IV)  $-140^\circ$ ,  $Si_2H_6$ ,  $H_2S$  and a little  $B_4H_{10}$ ; (V)  $-160^\circ$ ,  $H_2S$ ,  $CO_2$  and traces of  $PH_3$ ; (VI)  $-185^\circ$ ,  $SiH_4$  and a little  $CO_2$ . No hydride of B more volatile than  $B_4H_{10}$  could be detected in the crude gas. (5)  $B_4H_{10}$ , tension, 54 mm. at  $-40^\circ$ , 387 mm. at  $0^\circ$ ; m. p.,  $-120^\circ$ , b. p., 760 mm.,  $+18^\circ$ ; unstable, evolves H on standing. Si hydrides hasten decompn.; strong reducing agent, reducing higher Si hydrides to  $SiH_4$  and  $C_2H_6$  to a solid condensation product without formation of  $CH_4$ . (6)  $B_2H_6$ . Formed by heating  $B_4H_{10}$  in closed tube at  $90-95^\circ$ ; m.,  $-165.5^\circ$ ; b.,  $-92.5^\circ$ ; entirely stable in absence of moisture and fat. (7) Reaction of  $B_2H_6$  with halogen hydride:  $B_2H_6Br$ . (8)  $B_2H_6$ . From the mixt. earlier regarded as  $B_4H_{10}$ ; from 2 kg. of boride only 0.1 cc. liquid. M. p.,  $-46.9^\circ$ ; 0°-tension, 65 mm.; colorless, mobile, not very refractive, highly offensive odor; upon it chiefly depends the nauseating odor of B hydride mixts., not spontaneously inflammable when free from Si hydrides; slowly decompd. by water but otherwise much more stable than  $B_4H_{10}$  and  $B_5H_9$ . Later it was found that it could be obtained in somewhat larger yield by warming  $B_4H_{10}$  above  $100^\circ$ . (9)  $B_4H_{10}$ . From the same fraction as  $B_2H_6$ ; 1.5 cc. liquid from 2 kg. of boride. M. p.,  $-65.1^\circ$ ; 0°-tension, 7.2 mm.; colorless, highly refractive, not very mobile liquid, odor less pronounced than that of the other hydrides. Decomps. easily at room temp. to  $H_2$  and a yellow solid; reacts slowly with water and NaOH. (10) Yellow solid hydride from  $B_4H_{10}$ . The latter was allowed to stand in daylight at room temp. for several months and changed to thick brown-yellow slurr; volatile products were pumped off from time

to time. The yellow homogeneous cryst. residue had a compn.  $\text{BH}_{1.4}$ ; it dissolved completely in  $\text{C}_2\text{H}_4$ ; f.-p. lowering indicated about  $\text{B}_2\text{H}_6$ . (11) Decomposition of the hydrides by heat. All attempts to obtain a mono- and a triborane failed. Non-existence of  $\text{BH}_3$  is now made nearly certain. (12) Tabulation of properties of the boron hydrides at present known. (13) Action of Na-Hg on the hydrides. This caused condensations, still to be investigated, and not removal of H as in Si hydrides. (14) Action of  $\text{NH}_3$ .  $\text{B}_2\text{H}_6$  and  $\text{B}_4\text{H}_{10}$  both reacted to form liquid and solid products. No analyses. (15) Action of  $\text{C}_2\text{H}_2$ .  $\text{B}_2\text{H}_6$  and  $\text{B}_4\text{H}_{10}$  reacted little in the cold. Upon heating to  $100^\circ$  or quick compression explosive action took place with formation of brown solids. Gentle warming of the mixed gases formed condensation products of characteristic aromatic odor which evolved  $\text{H}_2$  from water. These could not be analyzed.

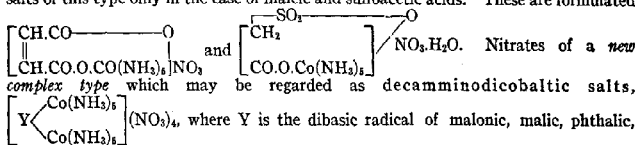
A. R. MIDDLETON

Complex metallic amines. VIII. Introduction of di- and tri-basic organic acid radicals into the pentamminocobaltic complex. J. C. DUFF. *J. Chem. Soc.* 123, 560-75 (1923); cf. *C. A.* 16, 1712.—Among the salts of the carbonatopentammino type, in which  $\text{CO}_3$  occupies only one coordination bond and which are customarily formulated



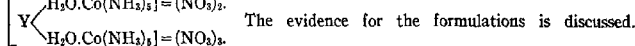
oxalate was the only dibasic org. radical previously known.

The results of attempts to introduce other dibasic org. radicals are here recorded. Reaction between the Na salts of the acids and  $[\text{H}_2\text{O}.\text{Co}(\text{NH}_3)_5](\text{NO}_3)_2$  gave salts of this type only in the case of maleic and sulfoacetic acids. These are formulated



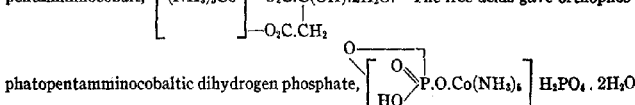
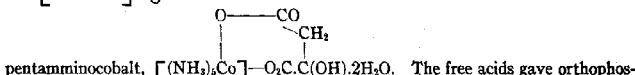
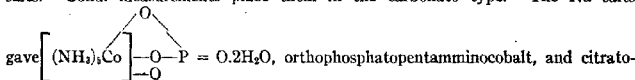
citraconic, itaconic, glutaric and adipic acids, and  $\left[ \begin{array}{c} \text{Co}(\text{NH}_3)_5 \\ | \\ \text{Y} \\ | \\ \text{Co}(\text{NH}_3)_5 \end{array} \right] \text{NO}_3$ , where Y

is the dibasic radical of mesotartaric and methionic acids, were obtained. Succinic, tartaric and fumaric acids gave only aquopentammino salts,

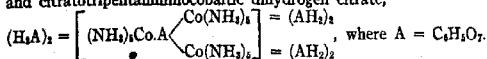


The evidence for the formulations is discussed.

Reaction between the acids and  $[\text{CO}_3.\text{Co}(\text{NH}_3)_5]\text{NO}_3$  gave salts of the above 3 types; maleic, sulfoacetic, phthalic and apparently mesotartaric gave salts of the carbonate type, distinguishable by the fact that they yield no ppt. with  $\text{K}_2\text{CrO}_4$ , except the mesotartarato compd. which is slowly converted to  $[\text{CrO}_4.\text{Co}(\text{NH}_3)_5]\text{NO}_3$ ; malonic, itaconic, citraconic, malic and glutaric acids gave salts of Type II which yield ppts. with  $\text{K}_2\text{CrO}_4$ ; succinic, tartaric, fumaric, adipic and methionic acids gave aquopentammino salts,  $[\text{H}_2\text{O}.\text{Co}(\text{NH}_3)_5]\text{Y}(\text{NO}_3)_2$ , converted by  $\text{K}_2\text{CrO}_4$  to  $[\text{CrO}_4.\text{Co}(\text{NH}_3)_5]\text{NO}_3$ . Orthophosphate and citrate radicals could be introduced into the pentammino complex by using the free acids and also their Na salts. Cond. measurements place them in the carbonate type. The Na salts



and citratotripentamminocobaltic dihydrogen citrate,



A. R. MIDDLETON

**Crystal examination of complex compounds.** H. STEINMETZ. *Z. Krist.* **57**, 233-52(1922).—The Werner octahedron and its crystallographic meaning are discussed, followed by a crystallographic study of combination of hexa-CN, Co, Fe, Cr, and Mn complexes with the  $NH_3$  complexes of Co and Cr. These compds. possess trigonal symmetry:  $[Co(CN)_6][Co(NH_3)_4]$ , reddish orange color,  $\alpha = 112^\circ 45\frac{1}{2}'$  ( $a:c = 1:0.4946$ ), sp. gr. 1.700;  $[Co(NH_3)_6][Fe(CN)_6]$ , orange yellow color,  $\alpha = 112^\circ 46'$  ( $a:c = 1:0.4943$ );  $[Co(NH_3)_6][Mn(CN)_6]$ , flesh red color, decomposes with  $H_2O$ ;  $[Co(NH_3)_4][Cr(CN)_6]$ , light orange yellow color,  $\alpha = 112^\circ 51\frac{1}{2}'$  ( $a:c = 1:0.4968$ );  $[Cr(NH_3)_6][Co(CN)_6]$ , yellowish color,  $\alpha = 112^\circ 46'$  ( $a:c = 1:0.4943$ );  $[Cr(NH_3)_6][Mn(CN)_6]$ , brownish yellow color,  $\alpha = 112^\circ 47'$  ( $a:c = 1:0.4939$ ), somewhat more stable than analogous  $Co(NH_3)_6$  salt;  $[Cr(NH_3)_4][Fe(CN)_6]$ , light orange yellow color,  $\alpha = 112^\circ 42'$  ( $a:c = 1:0.4968$ );  $[Cr(NH_3)_4][Cr(CN)_6]$ , very bright yellow,  $\alpha = 112^\circ 52'$  ( $a:c = 1:0.4906$ ). The above compds. show a rhombohedral cleavage. Replacement of  $NH_3$  by  $H_2O$  shifts the color from orange to red.  $[Co(NH_3)_4H_2O][Co(CN)_6]$ ,  $\alpha = 112^\circ 25\frac{1}{2}'$  ( $a:c = 1:0.4991$ );  $[Co(NH_3)_4H_2O][Fe(CN)_6]$ ,  $\alpha = 112^\circ 29\frac{1}{2}'$  ( $a:c = 1:0.4979$ ); brownish red;  $[Co(NH_3)_4H_2O][Cr(CN)_6]$ , brownish red,  $\alpha = 112^\circ 42\frac{1}{2}'$  ( $a:c = 1:0.4948$ );  $[Co(NH_3)_6][Co(NO_2)_6]$ ,  $[Co(NH_3)_6][Cr(CN)_6] \cdot 3H_2O$ , difficultly sol., crystal measurements not obtainable;  $[Co(NH_3)_6][Co(C_2O_4)_2] \cdot 3H_2O$ ,  $\alpha = 111^\circ 05'$  ( $a:c = 1:0.5528$ ), dark green color;  $[Cr \text{ urea}][Cr(C_2O_4)_2] \cdot 3H_2O$ , dark bluish green, triclinic symmetry,  $a:b:c = 0.6076:1:0.7079$ ,  $\beta = 99^\circ 15\frac{1}{2}'$ ;  $[Co(NH_3)_6][PtCl_6] \cdot 6H_2O$  and  $[Cr(NH_3)_6][PtCl_6] \cdot H_2O$ , small yellow crystals. PAUL BOONE

**Complexes of cobalt; experimental basis of the formulation of Werner.** P. JOH. *Bull. soc. chim.* **33**, 6-21(1923).—A lecture in which the chief facts of W.'s theory are clearly stated and their exptl. foundation is reviewed. A. R. M.

**Absorption of stannous chloride by stannic acid.** G. E. COLLINS AND J. K. WOOD. *J. Chem. Soc.* **123**, 452-6(1923).—With different modifications of stannic acid adsorption isotherms of ordinary type are obtained and at every concn. some  $SnCl_2$  remains unadsorbed. More Sn than Cl is taken up, probably part of the former as  $Sn(OH)_2$ . The  $\beta$ -acid showed more pronounced absorptive power; some factor other than size of grain is involved. The adsorptive power of the acid was less in presence of HCl. A stannous stannate would be somewhat decompd. by HCl and the acid tend to be resolved into modifications of less condensation and consequently lower adsorbing power for  $SnCl_2$ . A. R. M.

**Metal hydrides. Electrolytic formation of stibine in sulfuric acid and in sodium hydroxide solution.** H. J. S. SAND, E. J. WEEKS AND S. W. WORRELL. *J. Chem. Soc.* **123**, 456-70(1923).—Full description of methods and app. is given. Overvoltage was detd. by measuring "polarization" with a rotary commutator. The data and curves show that for an electrolyte of given compn. and temp. overvoltage becomes practically independent of c. d. after a "critical value" has been reached. Below this no  $SbH_3$  is produced, above it the yield is only slightly influenced by increase of c. d. The crit. values were about 8 milliamp. per  $cm.^2$  in acid and 11 milliamp. per  $cm.^2$  in alk. soln. The curves in acid and in alk. soln. are very similar; both show for low concns. very high overvoltages but little  $SbH_3$ ; with increased concn. of acid or alkali the overvoltage decreases to a value nearly const. for each temp. and the yield slowly increases. It is concluded that acid and alkali act as catalysts and in agreement with this some  $SbH_3$  is decompd. in the most acid solns. and in all the alk. ones. With rise of temp. overvoltage decreases and the yield of  $SbH_3$  becomes smaller and finally zero. The most favorable conditions are a compact Sb electrode in acid about 4 N, low temp. and c. d. above 10 milliamp. per  $cm.^2$ ; the yield is about 15% by vol. The free energy of the reaction  $2Sb + 3H_2 = 2SbH_3$  was calcd., with good agreement in acid and alk. soln., as about 62 cal. per 2 mols. of Sb at  $90^\circ$  and for  $20^\circ$  74.2 cal. in acid and 77 cal. in alk. soln. These are regarded as probably somewhat too high. A. R. M.

**Inorganic complex salts. II. Erdmann's salt and its derivatives.** WM. THOMAS. *J. Chem. Soc.* **123**, 817-9(1923).—The product of the action of oxalic acid on Erdmann's salt was converted into the Ba salt which by fractional crystn. was sep'd. into rhombohedral and monoclinic isomerides, the former more sol. and abundant (4:1). The former only could be resolved into optical isomers, indicating that it is the *cis*-dinitro-*cis*-diammino compd. and that the monoclinic form is the *trans*-dinitro-*cis*-diammino compd. Equiv. quantities of the Ba salt and strychnine sulfate were mixed in soln. and subjected

to fractional crystn. The active salts were converted by aq. KI into the active K salts which had  $[\alpha]_D = +154^\circ$ , whence  $[M]_D = 4815^\circ$ . Brucine and cinchonine proved unsuitable, hydrolysis resulting in pptn. of the free base. *d*-Phenylethylamine gave the *d*-complex salt in the first fraction. The corresponding malonate deriv. was prepd. but could not be resolved. Attempts to prep. a dioxalato and a dimalonato deriv. did not succeed. This work indicates Erdmann's salt to be a *cis*-compd. contrary to the conclusion of Riesenfeld and Clement (*C. A.* 17, 503).

**Hypophosphorous acid.** V. Its reaction with silver nitrate. A. D. MITCHELL. *J. Chem. Soc.* 123, 629-35(1923); cf. *C. A.* 16, 3822.—Under similar conditions  $\text{AgNO}_3$  is reduced at the same rate as  $\text{I}_2$ ,  $\text{HgCl}_2$  and  $\text{CuCl}_2$  independent of concn. provided this exceeds 0.02 *N* in case of  $\text{AgNO}_3$ . As in the previous cases the formation of an active form of the acid appears to be involved. The uniformity of the reductions studied and the definite evidence that the change is reversible are believed to be strong evidence for tautomerism in an inorg. acid, this being the first established case among such compds.

**Higher oxide of nickel.** O. R. HOWELL. *J. Chem. Soc.* 123, 669-76(1923); cf. *C. A.* 17, 1394.—Hypochlorites free from alkali react with  $\text{NiSO}_4$  at a rate negligible in comparison with that in presence of alkali. With excess of alkali the pptd.  $\text{Ni}(\text{OH})_2$  is oxidized quant. beyond  $\text{Ni}_2\text{O}_3$  but, owing to catalytic decompn. by the peroxide formed, larger amts. of hypochlorite produce only a small proportionate increase in the O content. With  $\text{Na}_2\text{CO}_3$ , hypochlorites oxidize similarly the  $\text{NiCO}_3$  but liberated  $\text{CO}_2$  forms bicarbonate of Ni and pptn. is incomplete. The ppt. is very unstable and evolves O even in suspension at ordinary temp. Decompn. proceeds beyond the  $\text{Ni}_2\text{O}_3$  stage; the rate is retarded by alkali. Increased rate of decompn. at higher temps. results in a lower O content of ppts. at these temps. The O content increases at higher concns. of the reacting substances, probably due to increased protective action of alkali.

**Nickel sulfide.** W. GLUUD AND W. MÜHLENDYCK. *Ber.* 56B, 899-901(1923); cf. *C. A.* 16, 2087, 3278.—Of the sulfides which might be expected to oxidize in  $\text{NH}_3$  soln. like  $\text{CuS}$ , viz.,  $\text{Zn}$ ,  $\text{Cd}$ ,  $\text{Co}$ ,  $\text{Mn}$  and  $\text{Ni}$ , only the last behaves analogously to  $\text{CuS}$ . The reactions proceeds more rapidly and smoothly than with  $\text{CuS}$  and with S as the chief product; only a little sulfate and thiosulfate are formed.  $\text{NH}_3$  concn. and age of the sulfide had no influence.

**Silicon hydrides.** XIV. Trichloro- and tetrachloro-monosilane,  $\text{SiHCl}_3$  and  $\text{SiCl}_4$ . ALFRED STOCK AND F. ZEIDLER. *Ber.* 56B, 986-97(1923); cf. *C. A.* 17, 1392.— $\text{SiHCl}_3$  was prepd. from com.  $\text{Cu}_2\text{Si}$  and  $\text{HCl}$  at  $300^\circ$ ; from the volatile products at  $-85^\circ$  a mixt. of  $\text{HCl}$ ,  $\text{SiHCl}_3$  and much  $\text{SiCl}_4$  was sepd. From this everything volatile at  $-125^\circ$  was removed and from the residue  $\text{SiHCl}_3$  sepd. by repeated fractional distn. and condensation, m. p.,  $-126.5^\circ$ ; 0° tension, 218 mm.; b. p.,  $760\text{ mm.}, 31.8^\circ$ . Vapor of  $\text{SiHCl}_3$  was led very slowly through a porcelain tube; decompn. began at  $400^\circ$  but was nearly complete only at  $900^\circ$ ; products,  $\text{Si}$ ,  $\text{HCl}$ ,  $\text{SiCl}_4$  and traces only of a liquid less volatile than  $\text{SiCl}_4$ . Freshly sublimed  $\text{AlCl}_3$  did not react at all with  $\text{SiHCl}_3$  in 48 hrs. at  $175^\circ$ . Na-Hg reacted readily at room temp., apparently by according to  $\text{SiHCl}_3 + 3\text{Na} = 3\text{NaCl} + (\text{SiH})_2$ ; the  $\text{SiHCl}_3$  vanished without formation of other volatile products. With excess of  $\text{NH}_3$  at 0.25-0.33 atm. and  $60-70^\circ$   $\text{SiHCl}_3$  reacted readily, forming solid colorless  $[\text{SiH}(\text{NH})_2]\text{NH}_3$  and  $\text{NH}_4\text{Cl}$ . The imide is quite stable; upon warming to  $150^\circ$  in vacuum it slowly decompd., forming chiefly  $(\text{SiHN})_2$ , and  $\text{NH}_4\text{HCl}$  converts the imide chiefly to  $\text{SiHCl}_3$ . Action of  $\text{NH}_3$  on  $\text{SiCl}_4$  gives not  $\text{Si}(\text{NH}_2)_4$  but diamino-imino-monosilane, according to  $\text{SiCl}_4 + 7\text{NH}_3 = \text{Si}(\text{NH}_2)_2\text{NH} + 4\text{NH}_4\text{Cl}$ . On warming in vacuum to  $0^\circ$  the amino imide formed  $\text{Si}(\text{NH}_2)_3$ .  $\text{SiHCl}_3$  reacted at once with water, forming dioxo-disiloxane,  $[\text{SiH}(\text{O})]_2\text{O}$ , in polymeric, solid, non-volatile form.

**Some new compounds of platinum, palladium, iridium, and rhodium, and a new method of determining them.** V. N. IVANOV. *Chem.-Zig.* 47, 209-10(1923).—The characteristic complex compds. of the Pt group do not ppt. out from soln. but sep. as crystals on evapn. of the solns. Under ordinary conditions with relatively concd. solns. Pt, Pd, and Rh form double thiocyanates of the type formula:  $\text{Pt}(\text{CNS})_2 \cdot 2\text{KCNS}$ . In very dil. solns., however, the double thiocyanates do not form. Pd separates in the form of a reddish-brown, amorphous ppt. similar to  $\text{Fe}(\text{OH})_3$ . Pt and Rh give no ppt. but are present as colloids, precipitable either by electrolytes or by dialysis in 2% agar-agar soln. **Platinum thiocyanate.**—The simple thiocyanate of Pt is obtained by adding a 0.25%  $\text{NaCNS}$  soln. to 0.25%  $\text{K}_2\text{PtCl}_4$  soln. On standing 5-6 hrs. at room temp. the  $\text{Pt}(\text{CNS})_2$  is pptd. by adding 50 g.  $\text{NH}_4\text{NO}_3$  or other nitrates or sulfates to each l. of soln. and the latter shaken vigorously. A ppt. similar to  $\text{Fe}(\text{OH})_3$  is obtained,

washed with cold water, and dried over  $P_2O_5$ . Prolonged washing, especially with warm  $H_2O$ , and drying at higher temps. lead to hydrolysis. The dried mass consists of glistening dark-brown particles. *Platinum dithiocarbamide tetrahydrosulfide*.—A 0.25% soln. of  $K_2PtCl_6$  is twice evapd. with  $HNO_3$ , and the residue diluted to the same original concn. The soln. is then heated to boiling in a 1-l. beaker and a 0.25% NaCNS soln. added 1 cc. at a time, while the soln. is kept boiling. One g. Pt requires about 250 cc. NaCNS soln. Heating is discontinued, 20 g.  $NH_4NO_3$  added and again boiled for several mins. The voluminous black ppt. is filtered off and dried. It is sol. in KCN and aqua regia, and gives off HCN on continued boiling. On ignition Pt remains as residue, affording a quant. method of detn. The ppt. contained Pt 76.88, S 9.97, C 2.07, N 2.63, H 0.82, and O 7.61%, corresponding to the formula  $Pt_4(OH)_4S(CSNH_2)_2$ . A comparison of the use of this compd. for detg. Pt quantitatively shows it to be fully as accurate and far more rapid than the chloroplatinate method. As for the other Pt metals, Pt and Rh both form this definite compd. Ir yields a yellow ppt. of variable compn. Os and Ru do not form corresponding compds. under these conditions. *Dithiocarbamide palladium sulfide*.—This compd. is prepd. from  $K_2PdCl_4$  in the same manner as the foregoing Pt compd. but without the necessary addn. of electrolytes. The Pd compd. is a dull-black mass, sol. in KCN and aqua regia, and decomposes on ignition to an easily fusible sulfide of Pd. The ppt. on analysis gave: Pd 63.57, S 25.06, C 5.00, N 5.51, H 0.057%, corresponding to the formula  $Pd_3S_2(CSNH_2)_2$ . The low-melting product on ignition was identified as a sulfide of Pd approximating  $Pd_2S$ , but of uncertain compn. owing to oxidation of some S during the ignition. I. has employed this Pd-S alloy in repairing cracked Pt-crucibles with success. The Rh compd. is similar to that of Pd, but in its prepn. an excess of NaCNS prevents complete pptn. and on ignition it does not yield the fusible sulfide similar to Pd. The compn. of the Rh compd. has not been definitely established. Equations are given to represent qualitatively the reactions taking place in the formation of these compds.

T. F. BUEHRER

**Anodic formation of a perchloride of manganese.** A. N. CAMPBELL. *J. Chem. Soc.* 123, 892-4(1923).—Electrolysis of 3*M*  $MnCl_2$  (anolyte) and  $NH_4Cl$  (catholyte), 250 g. per l., in a diaphragm cell between Pt electrodes with an anodic c. d. of 6 amp./dm.<sup>2</sup> yielded a dark soln. contg. only  $MnCl_2$  and unchanged  $MnCl_2$ . The normal potential of  $Mn^{++}$  in the presence of  $Mn^{+++}$  has been calcd. from oxidation-reduction potential measurements, whence  $E_{Mn^{+++}/Mn^{++}} = 1.465$  (H scale) at 18°. H. J. C.

**Action of solutions of alkali hydroxides on cupric oxide and on copper, and the existence of salts of cupric acid.** H. J. M. CREIGHTON. *J. Am. Chem. Soc.* 45, 1237-43(1923).—Blue solns., identical in behavior, were prepd. (1) by dissolving  $Cu(OH)_2$  in concd. alkali hydroxide; (2) by digesting  $CuO$  in concd. alkali hydroxide at 80-90°; and (3) by electrolyzing concd. alkali hydroxide between Cu electrodes at 80-90° with high c. d. These blue solns. do not exhibit the characteristic properties of colloidal solns., particularly those of colloidal  $Cu(OH)_2$  prepd. by Ley. Evidence is set forth that the blue color is due to presence of cuprate anion. The soly. of alkali cuprates in alkali hydroxide is small but increases rapidly with concn. of the alkali hydroxide. The K salt appears to be more sol. than the Na salt. A. R. MIDDLETON

**The reaction between hypochlorite and potassium iodide.** I. M. KOLTHOFF. *Rec. trav. chim.* 41, 815-26(1922).—The reaction between hypochlorite and iodide can be used analytically for the detn. of the value of Ca hypochlorite and other hypochlorites. If hypochlorite is titrated according to Pontius (*Chem.-Zig.* 28, 59(1904)) with iodide in bicarbonate soln. the iodide is oxidized completely to iodate. At the end of the titration a drop of excess iodide soln. reacts with the formation of I which can be detected with starch. The question is how is the formation of I at the end of the titration to be explained. K. reviews the known facts and views concerning this reaction before describing his own expts. from which he concludes that  $HClO$  reacts with the iodide quantitatively in bicarbonate or faintly acid soln. thus:  $3HClO + I^- \longrightarrow IO_3^- + 3H^+ + 3Cl^-$  if the solns. are titrated slowly. This oxidation occurs by way of  $IO^-$ . If the titration is rapid not all of the  $IO^-$  can go over into  $IO_3^-$  and too much reagent is used. This occurs especially in faintly acid soln. The amt. of  $IO^-$  present can be detd. approx. by adding a large excess KI and titrating the  $I_2$  formed with  $Na_2S_2O_4$ :  $IO^- + I^- + 2H^+ \longrightarrow I_2 + H_2O$ . The velocity with which  $IO^-$  goes over into  $IO_3^-$  depends on the H-ion concn. of the soln. If the soln. is strongly alk. too much reagent is bound. In mineral acid soln. no color change with starch is perceptible because no  $I^-$  ions remain in the soln. to form starch iodide. In  $H_2SO_4$  and HCl soln. Cl compds. as well as  $IO_3^-$  are formed. Andrews, *Z. anorg. Chem.* 36, 77 (1903) thus:  $I^- + 2Cl \longrightarrow ICl + Cl^-$  and react thus:  $ICl + 4Cl + 3H_2O \longrightarrow$

$\text{IO}_3^- + 6\text{H}^+ + 5\text{Cl}^-$ . The latter reaction is reversible and only goes to completion toward the right at very high diln. or if the HCl formed is neutralized. The method of Klimenko (*Z. anal. Chem.* **42**, 718(1903)) for detg.  $\text{ClO}^-$  and Cl in the presence of each other does not give good results. In bicarbonate soln. Cl as well as  $\text{ClO}^-$  is titratable with iodide. The appearance of the first blue coloration with starch in titrating  $\text{ClO}^- + \text{I}^-$  is due to the reaction:  $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \rightarrow 3\text{H}_2\text{O} + 3\text{I}_2$ .

R. J. WITZEMANN

**Reaction of chromium, iron and aluminium in the presence of tartaric acid and of glycerol.** SHIN-ICHIRO HAKOMORI. *J. Chem. Soc. Japan* **43**, 629-47(1922).—By means of absorption spectra, elec. cond., ultramicroscope and colloidal behavior, H. studied the reasons why  $\text{NH}_4\text{OH}$  will not ppt. the hydroxides of Cr, Fe and Al in the presence of tartaric acid or glycerol. (I) Cr.—When 1 *N* Rochelle salt is mixed with *N* chrome alum, and  $\text{NH}_4\text{OH}$  is immediately added the hydroxide ppts. out in large quantity, but if the mixt. is left for a longer time before addn. of  $\text{NH}_3$ , it becomes a reddish purple and the hydroxide is no longer pptd. by  $\text{NH}_3$ . The reaction between Cr and Rochelle salt is therefore very slow. Spectroscopic analysis shows that if 1 atom of Cr is mixed with more than 7.5 mol. of Rochelle salt, all of the Cr enters into complex salt formation with Rochelle salt. By the spectroscopic method of Shibata for detg. the compn. of a complex salt, H. found the complex salt to consist of 1 atom of Cr and 1 mol. of tartaric acid. The acidity of the medium influences the speed of this reaction, which is also greatly hastened by heat. The curves of the elec. cond. of the cold mixt., the mixt. boiled for  $\frac{1}{2}$  min. and the mixt. heated for 30 min. at  $100^\circ$  show that without heating, there is no complex salt formed. The point at which the max. elec. resistance occurs corresponds to the mixt., whose ratio of the 2 components is such that spectroscopic analysis and pptn. of the hydroxide by  $\text{NH}_3$  indicate the absence of Cr ions. When tartaric acid is not present in sufficient quantity, an addn. of  $\text{NH}_3$  produces the colloidal hydroxide which was demonstrable by ultramicroscopic and salting out expts. (II). Fe and Al also form a complex salt with tartaric acid which contains 1 atom of the metal, and 1 mol. of tartaric acid. Ferric Fe is reduced on long standing. There is not enough evidence to show complex salt formation with Al and Cr with glycerol. With Fe, spectroscopic evidence was slightly in favor of complex salt formation when 1 Fe is present in 1145 mol. of glycerol. Failure of hydroxide to ppt. in the glycerol is therefore due to colloidal phenomena, induced by the high viscosity of the soln. S. T.

**The action of potassium cyanide on monochloramine.** W. F. SHORR. *Chem. News* **126**, 100-1(1923).—Instead of the reaction,  $\text{KCN} + \text{NH}_2\text{Cl} = \text{KCl} + \text{NH}_2\text{CN}$  taking place, S. finds that  $2\text{KCN} + 2\text{NH}_2\text{Cl} = 2\text{KCl} + \text{NH}_3 + \text{NH}(\text{CN})_2$ . It is probable that the dicyanamide is produced by the interaction of CN.CI with cyanamide, after the latter 2 compds. have been formed thus:  $\text{HCN} + \text{NH}_2\text{Cl} = \text{NH}_3 + \text{CN.CI}$ , and  $\text{KCN} + \text{NH}_2\text{Cl} = \text{KCl} + \text{NH}_2\text{CN}$ . To an approx. molar ice-cold soln. of NaOCl is added, first one equiv. of 0.5 *N*  $\text{NH}_4\text{OH}$ , then one equiv. of KCN in concd. soln., both through a capillary tube. Maintain temp. below  $5^\circ$ . After 5 hrs. in ice-chest add enough  $\text{NH}_4\text{OH}$  to sustain in soln. the  $\text{AgCN}$  formed by the subsequent addn. of  $\text{AgNO}_3$ . Glistening, white crystals of  $\text{AgN}(\text{CN})_2 \cdot \text{AgCl}$  from  $\text{H}_2\text{O}$ ; decompd. by HCl in ether soln. to form  $(\text{CN})_2\text{NH} \cdot \text{HCl}$ . The hydrochloride is converted to biuret by warming with  $\text{H}_2\text{O}$ ; cold HCl converts the Ag compd. to  $\text{NH}_3\text{CO.NH.CN}$ . By removing Ag from the Ag salt with  $\text{H}_2\text{S}$  in  $\text{H}_2\text{O}$  soln., and concg. *in vacuo* a gelatinous mass seps., probably an insol. amorphous polymer of dicyanamide. By neutralization of  $\text{H}_2\text{O}$  soln. of dicyanamide with NaOH and addn. of  $\text{AgNO}_3$  the true  $\text{AgN}(\text{CN})_2$  is formed.

M. O. LAMAR

**Existence of ammonium hydroxide in solution.** T. S. MOORE. *Chemistry & Industry* **42**, 343(1923).—Controverting Caven (*C. A.* **17**, 1913), M. cites his detns. for  $25^\circ$  of the consts.,  $\text{CNH}_4 \times \text{COH}^- / \text{CNH}_4\text{OH} = 3.41 \times 10^{-3}$  and  $\text{CNH}_4\text{OH} / \text{CNH}_3 = 1.15$  (*C. A.* **2**, 17).

A. R. MIDDLETON

**Thallos hydroxide.** R. DE FORCRAND. *Compt. rend.* **176**, 873-6(1923).—For a rapid method of prep.  $\text{TlOH}$  add to liquid colorless  $\text{EtOTl}$  its vol. of water, about  $4\text{H}_2\text{O}$  to 1  $\text{EtOTl}$ . The 3 mols. of water in excess entrain the  $\text{EtOH}$  and the liquids are absorbed by porous plates for 24 hrs. under a bell. The product consists of yellow microcryst. grains, retaining about 4% of water or, nearly,  $\text{TlOH} \cdot 0.5\text{H}_2\text{O}$ . At  $13^\circ$  heat of soln. in water found was 6.388 cal. (Thomsen, 6.312 cal.), indicating that the excess of water is not combined. The heat of hydration of  $\text{Tl}_2\text{O}$  was detd. at  $13^\circ$  by dissolving in  $\text{HF} + 600\text{H}_2\text{O}$  large yellow crystals of  $\text{TlOH}$ , prepd. by the classical method, and their dehydration product, black  $\text{Tl}_2\text{O}$ . Found: for 2  $\text{TlOH}$ , + 25.210 cal.; for  $\text{Tl}_2\text{O}$ , + 28.327 cal. The difference, 3.117 cal. (Thomsen, 3.231 cal. at  $17^\circ$ ) gives the heat evolved in fixation of liquid water on solid  $\text{Tl}_2\text{O}$ , or, for solid  $\text{H}_2\text{O}$ , + 1.744 cal. From this  $155^\circ$

is calcd. as the temp. at which the efflorescence tension is 760 mm., a number near that of the salt hydrates which effloresce in cool dry air. In spite of the great difference in the heats of formation of  $\text{Ti}_2\text{O}$  (+ 42.8 cal.) and of soln. of  $\text{Ti}_2\text{O}$  and  $\text{TiOH}$  from those of the alk. metals,  $\text{TiOH}$  once formed is a very strong base, and can be titrated with strong acids with phenolphthalein as indicator.  $\text{TiOH}$  soln. was satd. with various OH derivs., trimethylcarbinol, pinacone, cyclohexanol,  $\text{MeOH}$ ,  $\text{EtOH}$ , glycol, glycerol, phenol,  $\text{AcOH}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HF}$ . The heat evolved exceeded that for  $\text{NaOH}$  in all cases except  $\text{H}_2\text{SO}_4$  and most in the case of the alcs. A. R. MIDDLETON

Detection of the formation of complex salts in dilute solutions (SHIBATA, INOUE)

2. Electrochemical preparation of tin hydride (PANETH) 4.

BLANCHARD and PHELAN: *Synthetic Inorganic Chemistry*. 3rd ed. Rewritten and enlarged. London: Chapman and Hall, Ltd. 15s. Reviewed in *Chem. Trade J.* 72, 549(1923).

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Accuracy in volumetric analysis. R. R. W. *Chem. Age* (London) 8, 478-9(1923).—An elementary discussion of precautions that should be taken. W. T. H.

Sliding scales for the convenient titration of strong liquids by dilution and the use of aliquot parts. C. H. D. CLARK. *Analyst* 48, 211-2(1923); cf. *C. A.* 17, 1766, 2091. —The scale is now shown in circular form. W. T. H.

Standardization of solutions used in iodometry. S. POPOFF AND F. L. CHAMBERS. *J. Am. Chem. Soc.* 45, 1358-60(1923).—When  $\text{Na}_2\text{S}_2\text{O}_3$  soln. is standardized against pure  $\text{I}_2$  in a soln. contg. 140 cc. of water, 10 g. of  $\text{KI}$  and 15 cc. of 6  $N$   $\text{H}_2\text{SO}_4$ , the results agree within 1 part in 10,000 with a standardization made by an equiv. vol. of  $\text{KMnO}_4$  added to 100 cc. of 10%  $\text{KI}$  soln. and 15 cc. of 6  $N$   $\text{H}_2\text{SO}_4$ . If care is not taken to keep the acidity the same in both titrations the agreement is not so good and values may not check to within less than 2 parts in 1000. W. T. HALL

The use of coordination compounds in analysis. T. M. LOWRY. *Chemistry & Industry* 42, 462-5(1923).—The analytical chemistry of the metals of the 8th group in the periodic table has been revolutionized by taking advantage of the fact that these elements are extremely sensitive to the processes of coordination, which may be thrown entirely out of gear by the addn. or removal of one planetary electron. A very complete sepn. of  $\text{Ni}$  from  $\text{Co}$  may be made by reducing to the metallic state and heating in a current of  $\text{CO}$ ;  $\text{NiC}_2\text{O}_4$  is volatilized. In faintly acid solns.,  $\text{Ni}$  and  $\text{Co}$  may be sepd. by forming a complex nitrite or cyanide of tervalent  $\text{Co}$ . In this case the electrons in the outer shell of  $\text{Co}$  are made up to the no. present in the next inert gas by sharing electrons with coordinated groups. In the dioximes, the complex contains 2 electrons less than the no. required to make this total and these compd. can be used to effect a complete sepn. of  $\text{Ni}$ ,  $\text{Pd}$  or  $\text{Pt}$  from other metals. The presence of  $\text{H}$  and  $\text{O}$  in these complexes may afford a clue to the special value of these 3 metals in catalytic hydrogenation and dehydrogenation. W. T. HALL

The use of bromate in volumetric analysis. II. The influence of mercuric mercury upon bromic acid reactions. G. P. SMITH. *J. Am. Chem. Soc.* 45, 1417-22(1923).—Oxidation reactions with bromic acid usually result in the formation of free  $\text{Br}_2$  but if the soln. contains sufficient  $\text{Hg}(\text{ClO}_4)_2$  the reduction of the bromate goes farther and bromide is formed. Undissociated  $\text{HgBr}_2$  is the cause of this effect.  $\text{Hg}(\text{ClO}_4)_2$  prevents the reaction between bromate and bromide in acid soln. at the boiling temp. It prevents the reaction between chloride and bromate in hot, acid soln. It aids the oxidation of  $\text{Mn}(\text{NO}_3)_2$  to  $\text{MnO}_2$  in nearly neutral soln., the oxidation of  $\text{Cr}(\text{NO}_3)_3$  to chromate in neutral soln., the oxidation of  $\text{HNO}_2$  to  $\text{HNO}_3$  and the oxidation of oxalic acid; in all these cases the bromate is reduced to bromide. In the Volhard titration of chloride, the  $\text{AgNO}_3$  can be replaced by  $\text{Hg}(\text{ClO}_4)_2$ . W. T. HALL

Use of phosphorus in gas analysis. ABRAHAM HENWOOD. *Ind. Eng. Chem.* 15, 650(1923). Reply. AUGUST HOLMES. *Ibid.*—Polemical. Cf. *C. A.* 17, 1806. E. J. C.

A rapid method for the determination of moisture. C. C. ROBERTS. *Catalyst* 8, 13(1923).—Spencer (*C. A.* 15, 454) has devised 3 forms of elec. oven through which a



stream of hot air is conducted. The results here published show that 20 mins' drying in the Spencer oven gives results which require several hrs. with a steam-heated oven.

W. T. HALL

The testing of bleach liquor. R. E. GEGENHEIMER. *Textile Colorist* 45, 167-8; *Color Trade J.* 12, 131-2(1923).—A description of a simple app. for the approx. detn. of available Cl in bleaching solns. by the  $H_2O_2$  gas-buret method, in which the pressure generated by the Cl evolved gives a direct reading in g. available Cl per l. Also in *Paper Mill* 47, No. 9, 14, 16(1923).

CHAS. E. MULLIN

Evaluation of potassium iodide. H. MATTHES AND P. SCHUTZ. *Pharm. Ztg.* 68, 256-7(1923).—Introduce 10 cc. of a 1% soln. of the well dried sample into a glass-stoppered flask, add 5 cc. of a 2%  $NaNO_2$  soln. and 2 cc. dil.  $H_2SO_4$ . After a lapse of 5 min. during which the liquid is frequently agitated, gradually add 100 cc. of a 5%  $NaHCO_3$  soln. Titrate the I thus freed with 0.02 N  $As_2O_3$  soln., being careful completely to dissolve all the I by agitating the liquid, to the point where a faint yellow color persists, and finally in the presence of starch to a colorless soln. One cc. 0.02 N  $As_2O_3$  soln. = 0.00332 g. KI.

W. O. E.

Nitrogen determination by the Kjeldahl method. MAX HÄSSIG. *Mitt. Lebensm. Hyg.* 14, 101-2(1923).—The process is not hastened by the use of  $HgI_2$  and there is the disadvantage of the sublimation of the iodide in the neck of the flask (cf. Sborowsky, C. A. 16, 4156).

BURTON G. PHILBRICK

Qualitative scheme for detection of cyanamide and related compounds. G. H. BUCHANAN. *Ind. Eng. Chem.* 15, 637-40(1923).—The scheme provides for the detection of  $NH_3$  and  $NH_4$  salts, cyanamide, HCN and its salts, dicyanodiamide, guanidine and its salts, guanilyurea and its salts,  $HNO_3$  and nitrates, HCNS and thiocyanates, thiourea and urea. For details, the original paper must be consulted.

W. T. HALL

Volumetric determination of sulfurous acid and thiosulfuric acid by oxidation with bromine in the nascent state. C. MAYR AND J. PRYFUSS. *Z. anorg. allgem. Chemie* 127, 123-36(1923).—Difficulties in the titration of  $H_2SO_3$  with  $I_2$  are probably due to atmospheric oxidation, although other explanations have been given during the past 67 yrs. A mixt. of thiosulfate and sulfite can be analyzed by titrating one portion with  $I_2$  and another portion with a mixt. of bromate and bromide. In the first case the following reactions take place:  $SO_3^{--} + I_2 + H_2O \rightarrow SO_4^{--} + 2I^- + 2H^+$ ;  $2S_2O_3^{--} + I_2 \rightarrow S_4O_6^{--} + 2I^-$ . In the second case, the reactions:  $SO_3^{--} + Br_2 + H_2O \rightarrow SO_4^{--} + 2Br^- + 2H^+$ ;  $S_2O_3^{--} + 4Br_2 + 5H_2O \rightarrow 2SO_4^{--} + 8Br^- + 10H^+$ . To det. sulfite alone, use a liter flask with ground glass stopper carrying a dropping funnel and a delivery tube, both provided with stopcocks. Place 2 g. of KBr and a carefully measured vol. of  $N/5$   $KBrO_3$  in the flask and conduct  $CO_2$  through the app. for 20 mins. Finally heat the soln. to boiling, remove the flame and shut both stopcocks to create a partial vacuum in the flask. Allow the  $Na_2SO_3$  soln. to flow into the flask, rinse out the funnel with a little water and finally add 20 cc. of concd. HCl. Shake and allow to stand for 15 mins. Then add 1.5-2 g. of KI dissolved in a little water and shake well. Transfer the contents of the flask to a titrating flask and titrate the  $I_2$  liberated from the KI by the excess  $KBrO_3$ . To det. thiosulfate alone, proceed in exactly the same way. To det. sulfite and thiosulfite in the presence of one another, titrate one portion as above outlined and titrate another portion directly with standard  $I_2$  soln. If  $m$  represents the milli-equivalents of  $I_2$  soln. required in the latter titration,  $n$  the milli-equivalents 0.1 N  $I_2$  corresponding to the  $Br_2$  that reacted with sulfite and thiosulfite in the former case,  $x$  the milli-equivalents of sulfite (millimoles/2) and  $y$  the milli-equivalents of thiosulfate (millimoles), then  $y = (n - m)/7$  and  $x = m - y$ .

W. T. HALL

Determination of sulfur dioxide and sulfur trioxide in burner gases by means of the gas-absorption flask. H. KRULL. *Papierfabr.* 19, 93-5(1921).—K. gives results of his analysis of S gases by means of a Reich gas-absorption flask. The detn. is more rapidly made than with the Orsat app. and comparative results showed an av. difference of 2.2%.

C. J. WESS

The estimation of boric acid. W. W. DEERNS. *Chem. Weekblad* 19, 480-1(1922).—D.'s method of estg.  $H_3BO_3$  in presence of  $H_3PO_4$  by means of KI-iodate is simpler than the method proposed by Kolthoff (C. A. 17, 1398) of adding Na citrate and titrating with alkali, and the interference of Ca compds. is not apparent. The citrate method is not new, having been proposed by Littmann (*Chem.-Ztg.* 22, 691(1898)) and Pyl (C. A. 8, 2432).

J. C. S.

The determination of phosphoric acid in plant ashes. K. I. KYULYUMOV. *Rev. inst. recherches agron. Bulgare* 1, 170-8(1920).—The literature shows that there is some

question as to whether there is any danger of losing  $P_2O_5$  when a plant is burned. A series of careful expts. shows that there is no danger of such volatilization but there is a possibility of some compd. being formed which contains  $P_2O_5$  and is not easily attacked by  $HCl$  and  $HNO_3$ . After treatment of the ash with these acids, therefore, it is advisable to add a few drops of  $H_2SO_4$ . When this is done all of the  $P_2O_5$  is recovered provided the proper precautions are taken in burning the original material. W. T. HALL.

**Determination of carbon and hydrogen by means of a mixture of sulfuric acid and silver dichromate.** L. J. SIMON AND A. J. A. GUILLAUMIN. *Compt. rend.* 176, 1065-7(1923).—Substances which resist the attack of  $H_2SO_4$  and  $CrO_3$  (cf. C. A. 17, 40) can be successfully oxidized by a mixt. of  $H_2SO_4$  and  $Ag_2Cr_2O_7$ . Naphthalene, ethyl pyroracetate, butyl glycolate, rhamnose, inositol acetate, aspirin, methyl *p*-cresol-sulfonate and thymol were oxidized in this way. The C and H content can be detd. by measuring the vol. of gas formed with a known wt. of  $Ag_2Cr_2O_7$  and then measuring the vol. produced by the excess of  $Ag_2Cr_2O_7$  when treated with a pure substance such as methyl sulfate. In practice, however, it is more convenient to keep the vol. const. and measure the pressure developed with the vol. of gas kept constant at 100 or 200 cc. Formulas are given indicating how the % C and % H are obtained from these data. W. T. HALL.

**New method for the electrolytic separation and determination of halogens.** GEZA SCHAY. *Z. Elektrochem.* 29, 123-6(1923).—A quant. sepn. of the halogens as free elements can be brought about by electrolysis if they are immediately removed from the electrolyte by boiling and cathodic reduction is suppressed by having the area of the cathode very much smaller than that of the anode. A method, based on these considerations, has been developed for the quant. detn. of Br and I, and for the sepn. of Cl, Br and I. This method is accurate to within 0.1%. H. JERMAIN CREIGHTON.

**The estimation of iodine by sodium thiosulfate.** F. O. RICE, M. KILPATRICK, JR., AND W. LEMKIN. *J. Am. Chem. Soc.* 45, 1361-5(1923).—In titrating with I soln. some  $I_2$  is likely to be lost by evapn. unless special precautions are taken. It is recommended to have the soln. added so that it does not fall through more than 1 cm. of air. Two % KI soln. is nearly as effective as 4% KI soln. for preventing loss of  $I_2$ .  $Na_2S_2O_3$  soln. is stable and can be standardized at once if made up with doubly distd. water that has been boiled to remove dissolved gas. In titrating acid solns. of  $I_2$  it is advised to add phosphate or borate buffer soln. W. T. HALL.

**The detection of traces of stibine.** E. J. WEEKS. *Chem. News* 126, 275(1923).—By passing  $SbH_3$  through a narrow tube wet with  $AgNO_3$  soln. a brown stain of Ag is produced by a trace of  $SbH_3$ . W. T. HALL.

**The examination of firearms and projectiles in forensic cases.** A. LUCAS. *Analyst* 48, 203-10(1923).—On receipt of a firearm, first note condition of the interior, whether clean or foul, oiled or rusty and whether there is any odor at the muzzle end. Test for  $H_2S$  with test paper. Pour hot water down the barrel, using 20 cc. for a rifle or shot gun and half as much for a pistol. Pass the water through the weapon 2 or 3 times. Smell the water, test with phenolphthalein and with  $Pb(OAc)_2$  paper. Test portions with  $BaCl_2$  for  $SO_4^{--}$ ,  $K_3Fe(CN)_6$  for  $Fe^{++}$ , KCNS for  $Fe^{+++}$ , sulfanilic acid for nitrite and with phenolsulfonic acid for nitrate. Filter some of the soln., note color of residue and test for both kinds of Fe. To analyze a projectile, take 0.5 g. in several small Erlenmeyer flasks and heat with 5 g.  $(NH_4)_2SO_4$  and 10 cc. of concd.  $H_2SO_4$ . After the alloy is all attacked, cool, add to the contents of each flask 25 cc. of 10% tartaric acid and boil the diluted soln. Filter and wash the  $PbSO_4$  with 10%  $H_2SO_4$ . To the filtrate in Nessler tubes, add a satd. soln. of  $H_2S$  and note the color of the ppt. In many cases a quant. detn. of Pb, Sb and Sn is desirable. Considerable advice is given regarding the phys. examn. of the material. W. T. H.

**An analytical test for tin with the acid of the molybdenum blue reaction.** G. F. HÜTTIG. *Chem.-Ztg.* 47, 341-2(1923).—The reaction between molybdate and a dil.  $SnCl_2$  soln. is extremely delicate; a blue color is developed with less than 0.01 mg. of Sn. H. assumes that the blue is due to the formation of  $(MoO)_2(MoO_4)_3 \cdot 6H_2O$ . The color, however, varies with the concn. and acidity of the soln. and the reaction is useful as a test only when the soln. is very dil. and the  $NH_4$  molybdate reagent is freshly prepd. In the ordinary qual. scheme, the sulfides of As, Sb and Sn are treated with concd.  $HCl$ , which does not dissolve As sulfide. To test for Sn, take a little of this soln., boil off the  $H_2S$ , add some more concd.  $HCl$  and reduce with stick Zn for 1 min. Filter into very dil. molybdate soln. prepd. by taking 6 cc. of the acid molybdate soln. used for the phosphorus test, adding 3 cc. of 2 N NaOH and dilg. to about 1 l. If 0.1 mg. Sn is present, a blue coloration will be obtained. With Sb a green coloration may result which is not likely to be confused with the blue produced by Sn. When considerable

Sb is present a white ppt. forms but in all cases the special tests for Sb should be made. The method has been applied to the quant. detn. of Sn; the details will be published later.

W. T. HALL

**Determination of manganese by titrating in the state of phospho-permanganic acid.** MATHEVET. *Ann. chim. anal. chim. appl.* 5, 99-108(1923).—The method described is the same in principle as the persulfate method so frequently used in the routine analysis of steel and other alloys. It is recommended, however, to have considerable phosphoric and sulfuric acids present and to have the soln. fairly dilute. For steels contg. less than 0.2% Mn, weigh out 1 g. into a 250-cc. Erlenmeyer flask. Heat on the water bath with 25 cc. of a soln. contg. 80 g.  $H_3PO_4$  (d. 1.71) 90 g. concd.  $HNO_3$  and 300 g. concd.  $H_2SO_4$  in 1250 cc. of water. When the steel is all dissolved add 5 cc. of 0.1  $N$   $AgNO_3$  and boil at least 30 sec. Add 30 cc. of hot water, bring to a gentle boil and add very slowly a satd. soln. of  $(NH_4)_2S_2O_8$  until a purple soln. is obtained. Cool and titrate with standard  $As_2O_3$  soln. until a yellowish green end-point is obtained. When the Mn content is higher, it is advisable to make sure that enough  $H_3PO_4$  is present to form the permanganate-phosphate and that enough  $H_2SO_4$  is present to help the decompn. of the permanganate during the arsenite titration. In the analysis of cast Fe it is well to dissolve the metal in 25 cc. of 7  $N$   $H_2SO_4$  and then add enough  $HNO_3$  to oxidize the Fe. Then evap. to dryness, take up in water and filter off the carbonaceous residue. Boil, add 5 cc. of  $AgNO_3$  and 5 cc. of 30%  $H_3PO_4$  soln., continuing as with low-Mn steels. For steels contg. up to 15% Mn, dissolve 1 g. as in the case of ordinary steel. If the soln. evaps. nearly to dryness add only water. Transfer to a liter Erlenmeyer flask, add 300-400 cc. of water and boil. Add 5 cc. of  $AgNO_3$  soln. and 60 cc. of the original acid mixt. and continue in the usual manner. Of ferromanganese, dissolve 4 g. in 100 cc. of 7  $N$   $H_2SO_4$ . After the metal has dissolved, add  $HNO_3$  to oxidize the Fe, boil to expel nitrous vapors, cool to about 50° and filter through asbestos. Wash with hot water, dil. to 1 l. and take 50 cc. for the analysis. Add 5 cc. of  $AgNO_3$  soln., 5 cc. of 30%  $H_3PO_4$  soln. boil, add 350 cc. of water, and the persulfate, etc. as usual. W. T. HALL

**The volumetric determination of tellurium by the dichromate method.** V. LENHER AND H. F. WAKEFIELD. *J. Am. Chem. Soc.* 45, 1423-5(1923).—Te can be detd. by titration with  $K_2Cr_2O_7$  if the following precautions are taken: Use as sample 0.1-0.3 g. of Te in the quadrivalent state. The proper acidity is obtained by adding 10 cc. of concd.  $HCl$  to 200 cc. of soln. To the soln. add 1-5 cc. more  $K_2Cr_2O_7$ , than should suffice to convert all the Te to the hexavalent condition. After 30 mins. add a measured excess of standard  $FeSO_4$  soln. and titrate the excess with  $K_2Cr_2O_7$ , using ferricyanide as outside indicator. W. T. HALL

**Studies on the quantitative determination of praseodymium.** P. H. M.-P. BRINTON AND H. A. PAGEL. *J. Am. Chem. Soc.* 45, 1460-5(1923).—Expts. with ignited Pr oxalate indicate that  $Pr_6O_{11}$  is formed if the Pr salt is not contaminated with other rare earth. The element may be detd. volumetrically by dissolving the oxide in concd.  $HNO_3$  (1 cc. for each 0.1 g. of oxide), dilg. to 100 cc. and adding an excess of standard oxalic acid soln. Keep the mixt. warm for 30 mins. or more, neutralize with  $NH_4OH$  and filter. Titrate the excess oxalic acid with  $KMnO_4$  at 60-70° in acid soln. W. T. HALL

**The detection and determination of indium.** I. WADA AND S. AYO. *Rep. Inst. Phys. Chem. Research (Japan)* 1, 190-212(1922); *Sci. Papers Inst. Phys. Chem. Research* 1, 57-77(1922); *J. Chem. Soc. (Japan)* 44, No. 1.—Unlike the members of the W-Cb group,  $In(NO_3)_3$  solns. are not hydrolyzed to form a salt insol. in  $HNO_3$  by evap. to dryness and baking the residue at 120°. Indium also cannot be sepd. from other elements by distn. of the bromide or by pptn. of the chloride.  $In_2S_3$  by itself is not pptd. to any extent by  $H_2S$  in solns. which are 0.3  $N$  with acid. The sulfide, however, is likely to be dragged down by other sulfides and in pptg. the Cu group it is best to introduce  $H_2S$  into a soln. which is 0.6  $N$  acid, filter, dil. with an equal vol. of water and ppt. again with  $H_2S$ . The 2nd ppt. will contain some Pt, In, Rh and Lu sulfides but all of these elements will be present in the filtrate. When it is desired to sep. in from Bi, the greater part of the Bi should be removed by hydrolysis and the remainder by  $H_2S$  pptn. in 0.6  $N$  acid.  $NH_4OH$ ,  $(NH_4)_2S$ ,  $NaOH$ ,  $Na_2O_3$  and  $Na_2CO_3$  all ppt. gelatinous  $In(OH)_3$ , or a sulfide or a carbonate so that with these reagents, as well as in the treatment of the  $HCl$  soln. with ether, the In follows Ti and Zr. In the presence of tartrate ions, In can be pptd. as sulfide like Fe and thus sepd. from Ti and Zr. K. KASHIMA

**Notes on the detection and estimation of small amounts of platinum and palladium in the presence of large amounts of silver.** C. A. KNITTEL. *Can. Chem. Met.* 6, 179-80(1922).—In anode slimes from the electrolytic refining of Ag recovered from Co ores,

the presence of metals of the Pt group was suspected. An interesting account is given of how from about 250 g. of the slimes 0.38 mg. of Pt and 0.32 mg. of Pd were obtained and identified.

W. T. HALL

**A new form for determining nickel.** W. LÖFFELBEIN AND J. SCHWARZ. *Chem.-Ztg.* 47, 366-70 (1923).—By neutralizing with  $\text{Na}_2\text{CO}_3$  and adding oxalic acid,  $\text{NiC}_2\text{O}_4$  can be pptd. and weighed as  $\text{NiO}$  after ignition or titrated with  $\text{KMnO}_4$  in acid soln., provided no other metal that forms an insoluble oxalate is present and there is not much  $\text{NH}_4$  salt in the soln.

W. T. HALL

**Dinitrosoresorcinol as a reagent for the quantitative determination of cobalt in the presence of nickel and other metals of the iron group.** W. R. ORNDORFF AND M. L. NICHOLS. *J. Am. Chem. Soc.* 45, 1439-44 (1923).—If a soln. of  $\text{CoCl}_2$  or  $\text{CoSO}_4$  contg. about 0.03 g. of dissolved Co in 50 cc. and 1 cc. of  $\text{HCl}$ , d. 1.17, is treated with 300 cc. of a hot, aq., 0.1% soln. of dinitrosoresorcinol, a deep red color results but no ppt. is formed. The addn. of 10 cc. of 10%  $\text{AcONa}$  soln. causes the formation of a voluminous, brownish red ppt. which can be filtered and weighed after drying at  $125^\circ$ . The ppt. corresponds to the formula  $\text{Co}(\text{C}_6\text{H}_3\text{N}_2\text{O}_4)_2$ . Co can be detd. in the presence of Ni by this method but it is necessary to wash the ppt. with 50 cc. of 0.085  $N$   $\text{HCl}$  to remove Ni. A similar method succeeds in the detn. of Co in the presence of Mn, Cu and Fe, however, must be removed. The application of the method to the detn. of Co in alloy steel is shown.

W. T. HALL

**The determination of rare earths and their separation from other metals.** I. The application of hydrolysis to the separation of titanium, iron and aluminium. II. The separation of titanium from iron and aluminium with sulfosalicylic acid. L. MOSER AND E. IRANYI. *Monatsh.* 43, 673-7, 679-84 (1923).—The sepn. of trivalent Fe from quadrivalent Ti is practically impossible by hydrolysis but the sepn. of Ti from Al is comparatively easy as Gooch and others have shown. The colloidal nature and adsorption tendencies of pptd. Ti hydroxide and basic salts make it necessary to keep the soln. as acid as possible. A satisfactory sepn. of Ti from Al can be accomplished in a soln. which is about 0.48  $N$  with H ions and this acidity can be obtained with the aid of  $\text{HCl}$  and  $\text{KBrO}_3$  as in the following procedure: First det. the combined wts. of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  after pptn. with  $\text{NH}_4\text{OH}$  or otherwise. Fuse the oxides with  $\text{KNaCO}_3$  and dissolve the melt in 6  $N$   $\text{HCl}$ . Carefully neutralize the soln. with  $\text{NaOH}$ , using methyl orange as indicator and avoiding heat as much as possible. Add 20 cc. of 1.2  $N$   $\text{HCl}$  and wait until the cold soln. becomes clear. Add 1 g. of  $\text{K}_2\text{SO}_4$  and 1.5 g.  $\text{KBrO}_3$ . Heat and boil gently for 30 mins. Filter and wash with hot water. If any deposit remains on the walls of the beaker or bottom of the cover glass, dissolve it in a little concd.  $\text{HCl}$  and ppt. with  $\text{NH}_4\text{OH}$ . The results of 5 analyses with  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ , ranging from 0.0125 to 0.1560 g. gave values always within 0.6 mg. of the truth. The soln. should not contain more than 0.05 g.  $\text{Al}_2\text{O}_3$  per 100 cc. when the Ti is pptd. For sepn. Fe and Ti it is often recommended to ppt. the former as sulfide in a soln. contg.  $\text{NH}_4$  tartrate. In place of the tartrate the water-sol. sulfosalicylic acid can be used. To prep. this, treat 50 g. of pure salicylic acid with enough concd.  $\text{H}_2\text{SO}_4$  in a 300-cc. beaker to form a paste. Heat on the sand bath to effect sulfonation. With a slight excess of  $\text{H}_2\text{SO}_4$ , the entire mass sometimes becomes solid. Heat until it is liquid again and the color has become a dark orange or violet brown. Cool and stir to prevent the formation of a hard mass. Finally dissolve by the gradual addn. of water. Add  $\text{NH}_4\text{OH}$  until the violet color changes to yellowish green, a few drops of dil.  $\text{H}_2\text{SO}_4$ , and dil. to 500 cc. Use 50 cc. of this soln. in each analysis. To sep. Fe from Ti, fuse the weighed oxides with  $\text{K}_2\text{S}_2\text{O}_7$  and dissolve the melt in cold, dil.  $\text{H}_2\text{SO}_4$ . Add 50 cc. of the sulfonated salicylic acid soln. and  $(\text{NH}_4)_2\text{CO}_3$  until the opaque, violet-black soln. changes to a clear red. In a vol. of 200 cc. sat. with  $\text{H}_2\text{S}$  and filter, while keeping the filter full to prevent oxidation of the sulfide. Wash the pptd.  $\text{FeS}_2$  with water contg. 10 cc. of the sulfonated acid in 200 cc. of water. Ignite and weigh as  $\text{Fe}_2\text{O}_3$  or as  $\text{FeS}$  with the necessary precautions. To sep. Ti from Al, advantage can be taken of the fact that  $\text{NH}_4\text{OH}$  ppts. Ti as hydroxide and no Al if the soln. contains the sulfonated salicylic acid. The soln. should be boiled 5 mins. after the addn. of the  $\text{NH}_4\text{OH}$ . In the analysis of a mixt. of Fe, Al, and Ti, first det. the 3 together as oxides. Fuse with  $\text{K}_2\text{S}_2\text{O}_7$  and proceed as described to ppt.  $\text{FeS}_2$ . Add  $\text{NH}_4\text{OH}$  and boil 5 mins. to ppt. Ti. The latter ppt. should be dissolved in 50 cc. of concd.  $\text{HCl}$  and the pptn. of the Ti repeated. This gives a purer ppt.

W. T. HALL

**The analysis of steel. I. Carbon.** A. KROFF. *Z. angew. Chem.* 36, 192-7, 205-9 (1923).—A critical study of the various methods for detg. C leads to the following conclusions: (1) The direct combustion of Fe and C in  $\text{O}_2$  taking place between  $900^\circ$  and  $1100^\circ$ . For a rapid combustion it is advisable to keep the temp. at  $1100^\circ$ . (2)

It is advisable to furnish  $O_2$  rapidly while the combustion is taking place, even when easily reducible oxide is added to the charge to promote the oxidation. (3) It is advisable to place some  $CuO$  or  $ZnO$  over the steel in the combustion boat. The former acts as oxidizer but the latter more as flux. With  $ZnO$  present a better residue is obtained and there is less danger of injury to the porcelain or quartz combustion tube. (4) There is always a tendency for a little  $CO$  to be formed unless  $CuO$  or  $Pt$  catalyzer is placed in front of the sample. (5) To remove oxides of S it is advisable to pass the gas from the furnace through a concd. aq. soln. of  $CrO_3$ . (6) Soda lime, slightly moist, is recommended for absorbing the  $CO_2$ . For the volumetric detn. it is advisable to use a measured vol. of standard baryta soln. and titrate the excess in a filtered aliquot after the combustion. (7) The detn. of the vol. of  $CO_2$  formed requires so much attention to details that it is not advisable to use this method of analysis for rapid work. (8) To save time in the computation, it is well to take 2.73 g. of steel for analysis; then each 0.1 g. of  $CO_2$  will correspond to 1% C in the steel. W. T. HALL.

**Determination of inorganic impurities in organic compounds soluble with difficulty in water, such as sulfuric acid in picric acid.** T. S. PATTERSON AND K. L. MOUNGILL. *J. Soc. Chem. Ind.* 42, 211-2T(1923).—To det.  $H_2SO_4$  adsorbed by picric acid, scrubbing with steam 3 times for about 30 mins. gave 750 cc. of soln. contg. all of the  $H_2SO_4$ , whereas the usual method of digesting 10 g. of material with 1 l. of water gave lower results. Dissolving 100 g. of picric acid in 200 cc. of nitrobenzene and shaking 4 times with 80 cc. of water also gave satisfactory results. W. T. HALL.

**Analysis of gas mixtures containing methyl chloride.** R. H. MCKEE AND S. P. BURKE. *Ind. Eng. Chem.* 15, 578-9(1923).—Pass the gas, confined over Hg and mixed with sufficient  $O_2$ , into an explosion pipet contg. a glowing Pt spiral. This causes combustion of  $CH_3Cl$  to  $HCl$ ,  $H_2O$  and  $CO_2$ . Absorb the  $CO_2$  and  $HCl$  in  $KOH$  and note the diminution in vol. Rinse out the app. and titrate the chloride present by the Volhard method. W. T. HALL.

**Determination of formaldehyde in the presence of copper sulfate.** M. JAKES. *Chem.-Ztg.* 47, 386(1923).—*Fungicides and insecticides* often contain  $HCHO$  in the presence of Cu salt. Before attempting to det.  $HCHO$  by the usual  $H_2O_2$  method it is necessary to remove the Cu, as otherwise it will be reduced by the  $HCHO$ .  $K_4Fe(CN)_6$  has proved to be a satisfactory precipitant of the Cu. W. T. HALL.

**The determination of mucic acid.** E. O. WHITTIER. *J. Am. Chem. Soc.* 45, 1391-7(1923).—Mucic acid may be titrated with  $KMnO_4$  in a hot, boiling, fairly acid soln. It is best to add an excess of oxidizer, allow to stand 5 mins. and then treat with a known vol. of standard oxalic soln., finally titrating with  $KMnO_4$  to an end point. Tartaric and racemic acids can be titrated by the same method. It is necessary to standardize the soln. of  $KMnO_4$  against these same acids because they are not oxidized completely to  $CO_2$ ; probably  $HCO_2H$  is an intermediate product which is partly volatilized. A mixt. of mucic and oxalic acids may be analyzed by titrating with 0.05 N  $KMnO_4$  at  $50^\circ$  whereby only oxalic acid is oxidized and then titrating the mucic acid at the boiling temp. W. T. HALL.

**A reaction of allantoin applicable to its determination.** J. MORE. *J. pharm. chim.* 27, 209-14(1923).—A soln. of allantoin (A) reduces Nessler's soln. with gradual pptn. of Hg (ous) salt; the reaction is sensitive to 0.001 g. per 10 cc. The reduced Hg (ous), after 12 hrs. standing may be detd. by 1 soln. (C. A. 16, 3281).  $I_2$  is equiv. to 1 mol. A, but as quant. detns. yield only 92%, a correction factor of 1.08 must be used. S. WALDBOTT.

**Adaptation of the iodometric aldose determination to the analysis of mixtures containing carbohydrate.** I. M. KOLTHOFF. *Pharm. Weekblad* 60, 394-402(1923).—Detailed directions are given for the detn. of lactose in milk after removal of the proteins by freshly pptd.  $K_2ZnFe(CN)_6$ ; glucose in invert sugar; and the successive detn. of glucose, fructose, sucrose and dextrin in potato sirup. Also in *Z. Nahr. Genussm.* 45, 141-7(1923). A. W. DOX.

**Kahlenberg's color reaction of cholesterol with arsenic trichloride.** E. ARBENZ. *Mitt. Lebensm. Hyg.* 14, 100-1(1923); cf. C. A. 16, 2315.—Since the cholesterol must be isolated in a pure state to give the rose-red color with  $AsCl_3$ , there seems little advantage in this method. BURTON G. PHILBRICK.

Some new compounds of Pt, Pd, Ir, and Rh, and a new method for determining them (IVANOV) 6. Catalytic decomposition of hydrogen peroxide in a bromine-bromide solution [determination of hydrogen peroxide] (BRAY, LIVINGSTON) 2. Reaction between hypochlorite and KI (KOLTHOFF) 6.

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## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

**The isomorphism of albite and anorthite.** F. ZAMBONINI. *Rend. accad. Lincei* 31, 295-301(1922); *Am. Mineral.* 8, 81-5(1923).—Z.'s views concerning the relations of at. diams. to certain types of isomorphism are essentially identical with those of Wherry (*C. A.* 16, 3047; 17, 947). In the change from albite to the isomorphous anorthite, a CaAl group is substituted for NaSi. This may occur without a distortion of the structure because the at. diams. of Ca and Na, and Al and Si, are very nearly equal, according to Bragg. Z. cites other examples of this volume isomorphism: diopside and acmite,  $\text{CaMgSi}_2\text{O}_6$  and  $\text{NaFe}^{++}\text{Si}_2\text{O}_6$ ; orthoclase and celsian, K and Ba feldspar; and the isogonism of triphylite and olivine,  $\text{LiFe}^{++}\text{PO}_4$  and  $\text{MgMgSiO}_4$ .

E. F. H.

**Volume isomorphism in minerals.** E. T. WHERRY. *Am. Mineral.* 8, 94-5(1923); cf. *C. A.* 17, 947.—The theory is suggested that in isomorphous series some set of elements of intermediate at. vols. may yield the most stable arrangement, and that the entrance of either larger or smaller atoms may cause a distortion of the structure, and change of symmetry. The stibnite group and related groups are cited as illustrations.

E. F. H.

**Structure and isomorphism in crystals.** R. W. G. WYCKOFF. *Am. Mineral.* 8, 85-92(1923); cf. preceding abstract, and *C. A.* 16, 3047; 17, 947.—Too few data are at hand to give an adequate explanation of isomorphous mixing. From present knowledge it is impossible to assume that the atoms of crystals are closely packed. The change in diam. of atoms from one compd. of an element to another is appreciable, invalidating any theory of *truly* const. at. radii. With some exceptions, the difference in size between various atoms of a crystal may not be greater than the change of diam. of the same atom in different sorts of crystals. Many replacements which should be possible on the theory of vol. isomorphism are not met with; e. g., a NaSi garnet. With low symmetry, as in the plagioclases, there are possible many structures nearly alike in at. groupings and unit cell dimensions. Albite and anorthite may have such structures, and the mixed crystals might be considered as mixts. of the albite and anorthite groupings, rather than as examples of at. replacements. At present no general and exact statement of the connection between isomorphism and at. arrangement can be made. The term *homeotaxial* (due to H. S. Washington) is proposed to describe crystals of similar compn. with sufficiently similar structures that they are crystallographically isomorphous.

E. F. H.

**The bismutiferous minerals of the province of Cordoba.** The presence of bismite. P. CASTRO-BARRA. *Bolet. r. soc. española hist. nat.* 21, 291-4(1921); *Mineralog. Abstracts* 2, 48.—Native Bi occurs in quartz at the San Jaime mine, district of Torrecampo. It is largely altered to greenish yellow bismite. Erythrite and heubachite are present to a less extent.

E. F. H.

**Orthoclase- and microcline-perthite and J. H. L. Vogt's phase diagram of potassium-sodium feldspar.** P. N. CHURVINSKII. *Z. Krist.* 57, 359-75(1922).—Quant. mineralogical seps. of some feldspars are tabulated. The av. analysis of the orthoclase, microcline, and cryptoperthite showed:  $\text{SiO}_2$  64.45,  $\text{Al}_2\text{O}_3$  19.65,  $\text{Fe}_2\text{O}_3$  0.63,  $\text{CaO}$  0.94,  $\text{K}_2\text{O}$  8.14, and  $\text{Na}_2\text{O}$  5.58%.

PAUL BOONE

**The chemical composition of fassaite from Hodrusbanja (Comitat Hont).** V. ZSIVNY. *Z. Krist.* 57, 387-93(1922).—Analysis gave:  $\text{SiO}_2$  48.56,  $\text{TiO}_2$  0.57,  $\text{Al}_2\text{O}_3$  9.06,  $\text{Fe}_2\text{O}_3$  1.68,  $\text{FeO}$  0.36,  $\text{MnO}$  trace,  $\text{MgO}$  14.89,  $\text{CaO}$  25.16,  $\text{Na}_2\text{O}$  0.09,  $\text{K}_2\text{O}$  0.04,

H<sub>2</sub>O 0.28%. A comparison of the above mineral with that from Fassatal discloses in the former 4.8% more SiO<sub>2</sub>, 3.6 more MgO, and 1.7 less FeO. PAUL BOONE

**Riebeckite from Vallone delle Minière (Valle della Germanasca).** E. GRILL. *Atti accad. Lincei* [v] 31, ii, 137-42 (1922).—Black crystals of riebeckite, up to 7 mm. in length and with submetallic luster and pronounced prismatic habit, were found on the eastern slope of Vallone delle Minière (Piedmont). They exhibit pleochroism and have d. 3.44; the angle (100):(110) is 55°5'-55°20'. Analysis gives: SiO<sub>2</sub> 51.53, TiO<sub>2</sub> trace, Al<sub>2</sub>O<sub>3</sub> 2.71, Fe<sub>2</sub>O<sub>3</sub> 16.22, FeO 17.11, MnO 0.22, CaO 0.79, MgO 1.01, Na<sub>2</sub>O 7.81, K<sub>2</sub>O 1.13, H<sub>2</sub>O—0.31, H<sub>2</sub>O+ 1.20, sum 100.04%, in accord with the empirical formula: 13SiO<sub>2</sub>·2(Fe,Al)<sub>2</sub>O<sub>3</sub>·4(Fe,Mg,Ca,Mn)O·3(Na,K,H)<sub>2</sub>O. J. C. S.

**Association of barylite and hedyphane at Långban.** G. AMINOFF. *Geol. För. Förh.* 45, 124-43 (1923); cf. C. A. 16, 2650.—Barylite occurs with hedyphane in thin tabular prismatic crystals 0.5 in. long; 2 cleavages at 84-90°; H. = 7; sp. gr. = 4.03. Its compn. is SiO<sub>2</sub> 35.51, BeO 16.1, BaO 47.43, CaO 0.42, MgO 0.21, PbO not detd., CuO not detd., Fe<sub>2</sub>O<sub>3</sub> 0.04, Al<sub>2</sub>O<sub>3</sub> 0.05, Bi<sub>2</sub>O<sub>3</sub> not detd., loss on ignition 0.57, sum 100.24%, indicating 2BeO·BaO·2SiO<sub>2</sub> or Be<sub>2</sub>BaSi<sub>2</sub>O<sub>7</sub>. A new analysis of material used by Blomstrand shows that what he detd. as Al<sub>2</sub>O<sub>3</sub> was really BeO. Six cuts and numerous tables give the results of the geometrical crystallography of 5 crystals studied. Crystals are rhombic and optically positive.  $p_0 = 1.0437$  (95 detns.) and  $g_0 = 0.8376$  (102 detns.) whence  $a:b:c = 0.8025:1:0.8376$ . Optical axis parallel with [100].  $V = 40^\circ 27'$ . Hedyphane occurs as transparent, prismatic crystals usually 1-2 mm., and as opaque pyramidal crystals about 1 cm. Both are light yellow. A gnomonic projection and 6 cuts are given. The crystals have the forms (0001), (1010), (1120), (1011), (2021), (1122), (1121) and (4152). W. SEGERBLOM

**Anderbergite from Ytterby.** G. K. ALMSTRÖM. *Geol. För. Förh.* 45, 119-23 (1923).—Brown anderbergite has the compn.: SiO<sub>2</sub> 21.55, P<sub>2</sub>O<sub>5</sub> 3.77, Ta<sub>2</sub>O<sub>5</sub> 6.53, ZrO<sub>2</sub> 28.67, rare earth oxides 14.31, Al<sub>2</sub>O<sub>3</sub> 1.75, ThO<sub>2</sub> 1.20, iron oxide 1.29, CaO 4.05, MgO 0.22, Na<sub>2</sub>O 2.44, K<sub>2</sub>O 0.53, H<sub>2</sub>O 11.97, insol. part 1.66, sum 99.74%; sp. gr. = 3.28. Black anderbergite has the compn.: SiO<sub>2</sub> 26.98, P<sub>2</sub>O<sub>5</sub> 3.32, Ta<sub>2</sub>O<sub>5</sub> 11.77, ZrO<sub>2</sub> 20.39, rare earth oxides 20.29, Al<sub>2</sub>O<sub>3</sub> 1.27, ThO<sub>2</sub> 1.00, Fe oxides 2.45, CaO 0.32, MgO not detd., Na<sub>2</sub>O 1.06, K<sub>2</sub>O not detd., H<sub>2</sub>O 11.61, insol. part not detd., sum 100.46%; sp. gr. 3.28. These analyses are compared with those of Nordenskiöld for the yellowish brown variety and of Blomstrand for the reddish yellow variety. The compn. varies with the color, the darker form being richer in Ta<sub>2</sub>O<sub>5</sub> and poorer in ZrO<sub>2</sub>. A. shows that xenotime and fergusonite are not the only foreign substances present. The foreign substance varies directly with the intensity of the color. The pure mineral is probably 8SiO<sub>2</sub>·6ZrO<sub>2</sub>·2CaO·R<sub>2</sub>O<sub>3</sub>·12H<sub>2</sub>O. The color varies from honey yellow and transparent to coal black and translucent. Streak on unglazed porcelain is nearly pure white for the light varieties and from light gray to brown or red for the darker varieties. The sp. gr. = 3.28-3.33, H. = 5.5-6. It is always accompanied by biotite and often by feldspar. W. SEGERBLOM

**The minerals of the southern Norwegian granite pegmatites. II. Silicates of the rare earths.** W. C. BROGGER, TH. VOGT, AND J. SCHETELIG. *Vid.-Selsk. Skrifter, Kristiana, I. Mat.-Nat. Kl. No. 1*, 151 + iv pp. (1922); *Mineralog. Abstr.* 2, 25-6.—*New observations on the crystal forms of hellandite.* W. C. Brogger (pp. 1-16). Eighteen forms and 3 types of twins are noted. *Thalenite from Rundholmen in northern Norway.* Th. Vogt. (pp. 17-47). Thalenite, previously known only from Sweden, is found in a feldspar quarry at Hundholmen. Reddish violet, transparent; monoclinic,  $a:b:c = 0.9190:1:0.6480$ ,  $\beta = 82^\circ 54.5'$  (new orientation); 23 forms were noted. Optical characters vary somewhat in different layers,  $\beta = 1.736$ , sp. gr. 4.454, H. 6-6.5. Analysis gave: SiO<sub>2</sub> 29.76, [Y(Ce)]<sub>2</sub>O<sub>3</sub> + traces of (Fe, Al)<sub>2</sub>O<sub>3</sub> and BeO 64.34, H<sub>2</sub>O 0.75. The formula is Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>. Optical data are given for associated orthite, orthite-epidote, and gadolinite. *Thortveitite, gadolinite, kainosite, and orthite.* J. Schetelig. (pp. 49-138). A complete description of thortveitite is given, with a history of scandium. A summary of occurrences, characters, and literature are given for orthite, kainosite, and gadolinite. Two new analyses of gadolinite are published, one with high Ce<sub>2</sub>O<sub>3</sub> (23.40%). *Supplement to part I.* J. Schetelig. (pp. 139-48). Notes on fergusonite, ilmenorutile, columbite intergrown with samarskite, euxenite, priorite (new analysis), risörite, alvite. E. F. H.

**The mineral tilasite at Långban.** G. AMINOFF. *Geol. För. Förh.* 45, 144-59 (1923); cf. C. A. 15, 220; 16, 2650.—Investigations on new tilasite material from Långban are recorded in 2 tables, 8 cuts of crystals and a gnomonic projection.  $a:b:c = 0.7436:1:0.8454$ ;  $\beta = 121^\circ 00'$ . New forms are (012), (113), (221), and (312). Optical prop-

erties are hard to det. New detns. of chem. compn. are, type A:  $\text{As}_2\text{O}_3$  50.91,  $\text{P}_2\text{O}_5$  trace, FeO 0.14, MnO 0.16, CaO 25.32, MgO 18.22,  $\text{H}_2\text{O}$  9.28, F 8.24, Cl 0.02,  $\text{Na}_2\text{O}$  0.20, sum 103.68, —F = O 3.47, sum 100.21%; sp. gr. = 3.78. Type B:  $\text{As}_2\text{O}_3$  51.13,  $\text{P}_2\text{O}_5$  0.10, FeO 0.21, MnO 0.05, CaO 25.69, MgO 18.12,  $\text{H}_2\text{O}$  0.43, F 7.45, Cl trace, insol. 0.08, sum 103.26, —F = O, 3.04, sum 100.22%; sp. gr. 3.76. Type C:  $\text{As}_2\text{O}_3$  48.33, MnO 0.15, CaO 25.27, BaO 9.62, MgO 17.32,  $\text{H}_2\text{O}$  0.07, F 7.95, insol. 2.61, sum 103.15, —F = O, 3.15, sum, 99.80%; sp. gr. = 3.79. The formula is probably  $(\text{MgF})\text{CaAsO}_4$ . The relation of tilasite to the wagnerite group is discussed. [The analysis-summations given appear to be erroneous. Abstr.] • W. SEGERBLOM

Recently described "bisbeeite" from the Grand Canyon is cyanotrichite. S. G. GORDON *Am. Mineral.* 8, 92-3(1923).—Optical and qual. chem. detns. show that a fibrous blue Cu mineral from the Grandview mine, described by Rogers (*C. A.* 16, 3837) as bisbeeite, is in reality cyanotrichite. E. F. H.

**Barytocelestite and apatelite from Spain.** P. CASTRO-BAREA. *Bol. r. soc. española hist. nat.* 22, 243-5(1922); *Mineralog. Abstracts* 2, 47.—Crystals of barytocelestite from near Jaén are described. Apatelite is noted as occurring at Ribesalbes, province of Castellón. E. F. H.

**Minerals of Andalusia.** P. CASTRO-BAREA. *Bol. r. soc. española hist. nat.* 18, 314-9(1918); *Mineralog. Abstracts* 2, 26.—Localities not previously recorded are given for 39 minerals from Andalusia. E. F. H.

**The composition of hofmannite.** G. BOERIS. *Rend. accad. sci. ist. Bologna* 25, 105-10(1921); *Mineralog. Abstracts* 2, 47.—Analyses by Ciusa of hofmannite (from the lignite of Siena), of bombicite, and hartite from Köflach, Styria all gave  $\text{C}_{20}\text{H}_{14}$ , with m.p. 75°. They are identical with hartite. E. F. H.

**A hydrocarbon of the lignite from Terni.** G. BOERIS. *Rend. accad. sci. ist. Bologna* 24, 120-5(1920); *Mineralog. Abstracts* 2, 47; cf. preceding abstract.—A whitish cryst. substance on lignite from Terni has m. p. = 74-5°, and an analysis by Ciusa (cf. *C. A.* 15, 2709) shows it to have the formula  $\text{C}_{20}\text{H}_{14}$ . The same results were obtained with bombicite (original material from Tuscany). Both substances are probably identical with hartite. E. F. H.

**The quantitative content of nickel-iron and troilite in meteoric stones.** P. N. CHIRVINSKII. *Bull. Inst. Sci. P. F. Lesgaft, Petrograd* 5, 111-5(1922); *Mineralog. Abstracts* 2, 34.—The percentages of nickel-iron and troilite recorded for 81 stones are tabulated. With increasing nickel-iron (0 to 25.83%) the amt. of troilite remains practically unchanged (at about 5-6%). E. F. H.

**The conception of vadose and juvenile and its significance in the study of ore deposits.** G. BERG. *Z. prakt. Geol.* 26, 23-8(1918).—The ideas of various authors concerning the terms vadose and juvenile are reviewed. From the surface downwards one meets the following boundaries: (1) the ground water level, (2) lower boundary of oxidation, (3) of weathering, (4) of vadose circulation, (5) between katamorphism and anamorphism. A distinction is made between truly juvenile (magmatic) waters and those set free in the metamorphism of sediments. Both types make up the water of thermal veins. E. F. H.

**The relations of primary vein minerals to one another and to igneous rocks.** G. BERG. *Z. prakt. Geol.* 27, 101-8, 118-25(1919).—The literature is summarized. A large diagram shows clearly the relations of associations of ore minerals to one another and to their parent igneous rock. It also indicates their position in the evolution from magmatic segregations through pegmatitic and pneumatolytic differentiations, and contact metasomatic deposits, to thermal veins. The same evolution is mineralogically represented by deposits in which the gang (1) contains feldspar, (2) is pure quartz, (3) is largely of fluorite, barite, and carbonates. Other diagrams present the distribution of the elements with respect to the parent rock and type of deposits in which they occur. Deposits of the following types are fully considered: Sn ores, Cu, Pb-Zn, Co-Bi, quartz-sulfide, Au-Te, Sb, Hg, Ti, apatite-Fe, pyrrhotite and the related types. Lastly the thermal metamorphism of ore deposits is treated. E. F. H.

**The distribution of metal content (copper, silver, molybdenum, and vanadium) in the Richelsdorf copper slate; a contribution to the genesis of ore beds.** P. KRUSCH. *Z. prakt. Geol.* 27, 76-84(1919).—The copper slates and associated sedimentary rocks near Richelsdorf contain: 2-6% Cu, 75 g./ton (and more) of Ag, 0.01-0.02% Mo, 0.04-0.05% V. The Cu ores in the slate form nests, concretions, and irregular fragments. The principal ores are chalcopyrite and cementation minerals. E. F. H.

**The upper Hessian basalt iron stone.** H. SIMONS. *Z. prakt. Geol.* 27, 140-7(1919).—Iron ores are formed by the alteration of a basalt. There are 3 types of primary, fragmental, ores: (1) strong concns. of limonite in placers, (2) concretions



in the clayey, entirely decompd., basalt, (3) concretionary formations in partially decompd. basalt. These ores are sometimes partially altered and rearranged by weathering. E. F. H.

The manganese-iron ores of Masca in the Siebenbürgen. H. QUERING. *Z. prakt. Geol.* 27, 133-40 (1919).—The ores near Masca were formerly worked. The ore bed is 10-40 m. thick, and extends for 2.5 km. It is made up of primary Mn-Fe carbonates and silicates, in the upper portion somewhat altered. Several analyses of unaltered ore give 23-33% Mn. The ore bed is a metamorphosed Mn-Fe sediment, and is surrounded by schists. E. F. H.

Occurrence and origin of white iron ore, a new raw material of iron. P. KRUSCH. *Stahl u. Eisen* 42, 1705-8 (1922).—A diagrammatic section through the white iron ore deposits in the western marshes of Germany is given. The pockets of ore occur in the lower marshes. Where they come to the surface they are colored brown, owing to the formation of  $\text{Fe}_2\text{O}_3$ . White iron ore which has been kept out of contact with air is almost pure ferrous oxycarbonate. After roasting the ore would contain 46-53% Fe. Micro-exam. shows that the ore consists of a gel contg. traces of spathic iron ore crystals. Available supplies amount to a few hundred thousand tons. The deposits are considered to have been formed by the deposition in water pockets of a colloidal soln. of ferrous oxycarbonate under the influence of humic acid but out of contact with the O of the air. Similar solns. formed in the presence of air have given rise to bog iron ore. J. S. C. I.

The manganese deposits of Hohenkirchen near Cassel. F. BREYCHLAG. *Z. prakt. Geol.* 27, 87-9 (1919).—These deposits are rather limited, but were formerly worked. The ore bed is 1.0-1.4 m. thick, and contains up to 15% Mn, with Fe, and is siliceous. It lies at the contact between a sandstone and Tertiary beds above. E. F. H.

The manganese deposits of Ukraine. K. CH. CHLERNIKOV. *Z. prakt. Geol.* 26, 89-92, 100-7 (1918).—Several occurrences of Mn ores are noted on the southern slope of the south Russian granite massif, in Ukraine. The geology of the deposit, analyses of the ores, and statistics are given. E. F. H.

Gold-bearing streams in the Hunsrück. A. ZÖLLER. *Z. prakt. Geol.* 27, 7-14 (1919).—Rich auriferous boulders occur sporadically in the beds of some Hunsrück streams. They are the remnant of cementation zones formed from sulfide veins poor in Au. Later these zones were broken up, and water containing humus acids leached out the finely divided Au, leaving the coarser particles. E. F. H.

Gold-bearing pyromorphite at Neu-Bulach in the Schwarzwald. A. SCHMIDT. *Z. prakt. Geol.* 27, 157-9 (1919).—An analysis of material from the dump of the old mines at Neu-Bulach showed, besides 1.6% Cu and 0.02% Ag, 0.0018-0.0021% Au. E. F. H.

The nickel-pyrrhotite occurrences at Ruda near Vingaker (East Götaland) in Sweden. SORG. *Z. prakt. Geol.* 27, 153-7 (1919).—The deposits at Ruda consist of Ni- (pentlandite), Cu- and Co- bearing pyrrhotite, in an unaltered norite, near its contact with gneiss. Analyses of the rock averaged 0.62% Ni, 0.44% Cu, and 0.03% Co. E. F. H.

Occurrences of tin ores in the Congo. F. BEUREND. *Z. prakt. Geol.* 27, 19-22 (1919).—Cassiterite-bearing pegmatites, and richer eluvial and alluvial placers occur in middle Katanga. The more important deposits are those at Muika (on the Luvua, south of Kiambi) and in the Bia Mts. E. F. H.

The molybdenum occurrences in middle Sweden. SORG. *Z. prakt. Geol.* 27, 35-43 (1919).—Mo deposits in the vicinity of Filipstadt, Ludvika, and Vestanfors are geologically described. Two types are noted: (1) veins along old tectonic lines, (2) garnet-skarn deposits with the ore irregularly distributed through the rock. The country rocks are metamorphic and igneous. E. F. H.

Barite in Mexico. E. WITTICH. *Bol. Minero (Mexico)* 13, 312-8 (1922); *Mineralog. Abstracts* 2, 32.—The modes of occurrence and localities of barite in Mexico are given. There are no com. deposits, and it is not abundant at any locality. E. F. H.

Matsap pan: a potential source of nitrates. A. W. ROGERS. *S. African J. Industries* 6, 73-80 (1923).—The brine from this pan contains an amt. of nitrate which might be of economic value with a large enough supply of brine. The supply must be tested. Analyses of the brine are given. It is a complicated mixt., and some of the Mg salts are very sol., which will cause some difficulty in obtaining a nitrate sufficiently free from other salts to sel. at the best price. The nitrates are probably derived from the soil in the catchment. E. F. H.

The Russian phosphorites. F. KAUNHOWEN. *Z. prakt. Geol.* 27, 71-8, 89-93

(1919).—A description of phosphorite deposits (1) near Grodno, (2) near Wolkowsk, (3) in the Kroljewetz district, (4) near Sumy, (5) in Podolien. In all cases the phosphate beds have accumulated at the base of a younger formation directly over an older one. Several analyses are given. E. F. H.

**Talc mining at Disentis in Graubünden.** ARN. HEIM. *Z. prakt. Geol.* 26, 2-11 (1918).—Details are given of the geology of several talc deposits. Two analyses of the primary periodotite from which the talc was formed by alteration are included. If the talc is ground, mixed with a binder, pressed, and heated to above 1200°, a very hard substance is obtained, which is used in Switzerland as a substitute for emery. Statistics conclude the paper. E. F. H.

**Memoir and map of localities of minerals of economic importance and metalliferous mines in Ireland.** G. A. J. COLA. *Mem. Geol. Survey Ireland, Min. Res.*, Dublin, 155 pp. (1922); *Mineralog. Abstracts* 2, 23.—The following are discussed: barite, bauxite, feldspar, gypsum, salt, steatite, Sb, Cu, Au, Fe, Pb, Mn, Mo, Ni, S, and Zn. E. F. H.

**The mineral occurrences of upper Italy.** G. BURTZ. *Z. prakt. Geol.* 26, 75-8 (1918).—The mineral resources of upper Italy include: Fe, pyrite, Cu, Pb, Zn, graphite, coal, S, oil, Mn, Au and building stones. E. F. H.

**The veins of the eastern Hartz.** A. STAHL. *Z. prakt. Geol.* 26, 97-100, 113-22, 130-9 (1918).—Mineral veins in the following districts are discussed: the Krum-schlachtal, in Auerberg, Neudorf-Strassberg, Harzgerode, Treseburg, Trautenstein, and easternmost Hartz. Veins of 3 periods predominate: (1) the oldest are fluorite-siderite veins with calcite and chalcopryrite; (2) then come quartz veins with sulfides of Fe, Cu, and more sparingly Ni, Zn, Pb, and Sb; (3) the youngest are barite-hematite veins. Their age and origin are treated. E. F. H.

**The mineral wealth of Estland.** F. BRYSCHLAG AND L. VON ZUR MÜHLEN. *Z. prakt. Geol.* 26, 141-50 (1918).—A discussion of the possibility of exploiting phosphate and oil resources. E. F. H.

**Sketch of the economic minerals of the Donets coal-basin.** P. N. CHIRVINSKII. *Bull. North Caucasian Meliorations, Novochebassk* No. 12, 193-204 (1919); *Mineralog. Abstracts* 2, 31.—This report deals with coal, phosphorite, salt, etc., gypsum, stone, and ores of Fe, Ag, Pb, Zn, Hg and Cu. E. F. H.

**Economic minerals of southeastern European Russia.** P. N. CHIRVINSKII. *Trans. of the Statistical-Economic Section of the Southeastern Union of the Unions of Credit and Lending Societies, Rostov on Don*, pt. 3, 1-84 (1919); *Mineralog. Abstracts* 2, 31.—Ores of Fe, Au, Ag, Po, Zn, Cu, Mn, Hg, Cr, Mo, As, Sb, S; coal, graphite, pyrite, phosphorite, fluxes, refractory and cement materials, stone, salt, etc., oil, gas, and mineral-waters are discussed. E. F. H.

**The mineral wealth of Turkey.** F. BRYSCHLAG. *Z. prakt. Geol.* 26, 81-8 (1918).—Deposits of the following minerals and ores are described: Fe (magnetite, hematite), corundum, Mn, chromite, Cu, pandermite, phosphates, coal (found in small amount), oil, asphalt. E. F. H.

**The mineral resources of the Philippine Islands.** H. FEHLINGER. *Z. prakt. Geol.* 27, 117 (1919).—Coal, oil, natural gas, gypsum, S, phosphates, stone, Au, Cu, Ag, and Pb deposits are briefly described. E. F. H.

**The ore deposits of the Dutch Indies.** G. BURTZ. *Z. prakt. Geol.* 27, 110-3 (1919).—Largely statistical. The resources comprise: coal, oil, Fe, Ni, Cr, Mn, Sn, and phosphates. E. F. H.

Brown coals of Victoria (HERMAN) 21. Crystal examination of complex compounds (STRINNETZ) 6. Crystal cleavage and crystal structure (HUGGINS) 2.

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## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, R. S. WILLIAMS

**Mining and metallurgical progress in Canada.** STOFFORD BRUNTON. *Can. Chem. Met.* 7, 119-20 (1923). E. J. C.

**Ore dressing, fluxes and fuels at Namtu.** R. G. HALL. *Eng. Mining J.-Press*

115, 712-15(1923).—Sixty-six % of the ore consists of intimate mixts. of sulfides as follows: PbS 30, ZnS 27, pyrite 6, other sulfides and arsenides 3%. The problem is one not of concn. but of sepn. of sulfide minerals. Fine grinding is essential for sepn. The milling plant is described. Ag mineral is not intimately associated with galena; Fe ore is essential to smelting.

**Theories on cupola reactions.** S. J. FELTON. *Foundry* 51, 351-2(1923).—By using an improved optical pyrometer, giving accurate temps. of molten Fe, F. has observed uniformly high temp. in a large no. of heats, in spite of certain variations in weather conditions, coke, pig scrap and charging. This is in direct contradiction to present theories on melting and superheating. A chart shows a temp. of 2800° F. at 26.5 in. above tuyères, 2784° at 18 in., 2911° at 12 in., 2893° at 6 in. and 2870° immediately above. The highest temp. is, therefore, 12 in. above the tuyères instead of 20 in. as claimed by Belden. F. believes that the lower the melting point of the pig, the higher in the stack will it melt and thus must traverse a greater distance to the tapping door. Its opportunity to superheat is thus increased, which tends to equalize pouring temps.

**The starting up of blast furnaces.** MAURICE DERCLAYE. *Rev. métal.* 20, 209-34 (1923).—D. discusses in detail the causes of troubles in starting up and how to avoid them, and describes the starting up of 6 different blast furnaces.

**The preparation of fused zirconium.** H. S. COOPER. *Trans. Am. Electrochem. Soc.* (advance copy) 1923.—ZrCl<sub>4</sub> was prepd. by passing Cl over ZrC, contg. some excess C, at a temp. of 500-550°. Reduction of the chloride was carried out with Na in a vacuum chamber, provided with an elec. heating coil. The temp. is raised to 500-600°, at which point the reaction starts and the temp. rises to 900-1000°. When cold the product is removed and the metal sepd. by floating off the fines with water. After it is cooled and dried a Zr metal of about 99% purity is obtained. The metal is only slightly attacked by concd. or dil. HCl or HNO<sub>3</sub> even when boiled therein. Hot concd. H<sub>2</sub>SO<sub>4</sub> dissolves it completely. Expts. indicate that the m. p. of Zr is about that of Mo, and very close to that of Ta, probably 2800°. Pyrophoric alloys are obtained with Sn when the Zr exceeds 60%, and with 70-80% equal the Ce-Fe alloys. Cutting tools, which retain their edge at red heat, are made with Zr up to 15%, some Al, W, Si, or Mo and a base of Ni. Zr-Ni alloys are ductile and machinable up to 5% Zr. Various other alloys of Zr with Mg, Au, Mn and W are being studied.

**Economic principles governing the use of electrical power in iron and steel works.** C. A. ABLETT. *J. Iron Steel Inst.* (London) (advance proof) 1923, 16 pp. E. J. C. Fatigue in metals. C. F. JENKIN. *Chem. Met. Eng.* 28, 811-5(1923).—A discussion of the possible technical application of Jenkin's ingenious fatigue test model to supplement test data.

**Quenching of soft steel from high temperatures.** M. SAUVAGNOT AND H. DELMAS. *Compt. rend.* 176, 1146-8(1923).—Extra soft steel (max. 0.1% C) has little quench power, i. e., its resistance is increased only a moderate amt. after quenching in cold water from 950°. Heating test pieces to higher temps. in an elec. furnace and then quenching in cold water showed, however, a considerable increase in resistance when the temp. exceeded 1350-1400°. Up to the fusion temp. the elastic limit, resistance, and hardness are considerably increased while the elongation and resilience are correspondingly decreased. Samples quenched at incipient fusion (about 1465°) were reheated for 15 min. to show a slight decrease in hardness at 300°, a rapid drop 300-400°, a gradual decrease 400-700°, and a very rapid drop in hardness at the crit. temp. 750°. Structurally samples quenched at 1350° are still ferrite and sorbite; at 1400° martensite and troostite; at 1450° and above, fine grained martensite.

**Hadfield's researches on special steel.** CARL BENEDICKS. *Teknisk Tids. Bergsvetenskap* 53, 25-30(1923).—A biographic sketch with portrait and a list of Robert Hadfield's publications on special steel.

**The mechanism of the corrosion of iron and steel in natural waters and the calculation of specific rates of corrosion.** R. E. WILSON. *Ind. Eng. Chem.* 15, 127-33 (1923).—Of the 3 fundamental reactions in corrosion, (1)  $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{++} + 2\text{H}$  (polarizing film), (2)  $2\text{H} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$  and (3)  $2\text{H} \rightarrow \text{H}_2$ , the first detrs. the rate of corrosion in strongly alk. solns., the second in solns. with a  $p_{\text{H}}$  roughly between 9 and 4, and the third in more acid solns. In the second range, which includes most natural waters and ordinary solns., the rate of diffusion of O to the surface is controlling, velocity and O concn. largely detg. the rate of corrosion. The  $p_{\text{H}}$  of the soln. and the compn. of the Fe or steel have a negligible effect. In the other ranges quite different factors control. This point of view reconciles many of the apparently contradictory results on corrosion and shows that most "accelerated" corrosion tests are likely to lead

to erroneous conclusions. Common misconceptions of the mechanism of "galvanic action" are discussed in detail.

E. J. C.

**Corrosion test on metals and alloys in acid water from coal mines.** W. A. SELVIG AND GEO. M. ENOS. Carnegie Inst. Tech. Coöperative Mining Courses, *Bull.* 4 (1922).—A highly statistical paper dealing with tests on 3 mine waters, the first of 119 days duration in water of Montour No. 1 mine contg. 1430 p. p. m.  $H_2SO_4$  and 11,360 parts  $H_2SO_4$  + sulfates of Fe and Al; the second of 135 days at Edna No. 2 mine, whose water showed 2160 p. p. m. in  $H_2SO_4$  and 14,160 p. p. m.  $H_2SO_4$  + Fe + Al sulfate; the third at Calumet mine with 430 p. p. m.  $H_2SO_4$  and 2950 p. p. m.  $H_2SO_4$  plus sulfates of Al and Fe. The flow of the water past the test-plates was 1.8 inches per min. Alloys of the brass type contg. considerable Zn showed considerable corrosion. Bronzes contg. Sn were corroded less. Cupro-Ni alloys were corroded similarly to the brasses. Ni-Ag alloys contg. Cu, Zn, and Ni were extensively corroded. Al alloys were pitted pronouncedly. The materials found highly resistant included a high Cr-steel, highly alloyed Cr-Ni-Si steels, a high-Si cast steel and a Ni-Cr-Fe alloy. These materials are hard and brittle or relatively expensive for general use in mines.

R. L. BROWN

**The inherent effect of alloying elements in steel.** E. D. SAKLATWALLA. *Trans. Am. Electrochem. Soc.* (advance copy), (1923).—A general discussion of the possible physico-chemical effects of the elements usually added to steel to make our commercial alloy steels. A plea for more scientific work to the end that the chem. properties of these elements may be coordinated with their physical effects upon steels.

W. E. RUDER

**The red-hardness of high-speed tool steel.** G. Z. NESSELSTRAUS. *Communications du Laboratoire Métallographique de l'Usine Poutiloff 1918; Rev. métal.* 20, (Extraits), 174-80 (1923).—N. studied the mechanism of red-hardness by means of thermal analysis, hardness tests, and photomicrography. Red-hardness is due to an exothermic transformation which takes place on heating the hardened metal. All steels which have been hardened in such a manner as to give austenite exhibit red-hardness at a point corresponding to an irreversible exothermic transformation. The corresponding variations in texture have the same general character and take place in the same order for all kinds of steel, provided they are due to the decompn. of austenite.

A. PAPINEAU-COUTURE

**The metals "Invar" and "Elinvar."** C. E. GUILLAUME. *Rev. ind. minérale* 44, 545-68 (1922).—An historical and technical outline of the development of *invar* and *elinvar* alloys, with their properties and uses.

C. C. DAVIS

**Special aluminium bronzes: aluminium bronzes containing phosphorus, magnesium and cobalt.** LÉON GUILLET. *Rev. métal.* 20, 257-61 (1923); cf. C. A. 17, 1615.—Even small amts. of P (0.2% or more) reduce the resiliency and elongation, and 0.6% considerably reduces the tensile strength. Mechanical tests and micrographic examn. both show that the addition of the slightest amt. of Mg causes formation of a compd. which must be  $Cu_2Mg$ . Al bronzes should not be deoxidized with Mg as a slight excess will make the alloy extremely brittle. Even small amts. of Co lower elongation and resiliency (Cf. Guillet, C. A. 15, 1483); but annealing generally softens the alloy and increases the resiliency. The compd. formed on adding Co (perhaps  $Al_3Co$ ) is not even partly destroyed by annealing. Addition of even slight amts. of Co is detrimental to the quality of the alloy.

A. PAPINEAU-COUTURE

**Electric welding of cast iron.** LEBRUN. *Rev. métal.* 20, 248-9 (1923).—In order to obtain a satisfactory elec. weld of gray cast Fe, means must be provided for continuous addn. of C to replace that burnt by the arc; otherwise the weld would be transformed into white cast Fe. Photomicrographs of both etched and unetched welds are shown.

A. PAPINEAU-COUTURE

**The X-ray examination of materials (WARREN) 13.** Crystal structure of Fe-Ni alloys (MCKERRHAN) 2. Röntgenographic determination of the structure of rolled metal foils (MARK, WEISSENBERG) 2. Oxidation of zinc sulfide by microorganisms (RUDOLFS, HELBRONNER) 11C. Ternary system, aluminium-zinc-tin (CREPAZ) 2. A new raw material for iron (KRUSCH) 8.

BARBEROT, A.: *La fabrication de l'acier au four Martin*. Paris: J. B. Baillières et Fils. 543 pp. Fr. 40. Reviewed in *Chimie et industrie* 9, 431 (1923).

JACQUET, ALFRED: *Aciers, Fers, Fontes*. Vol. I. 2nd Ed. Revised and enlarged. Paris: Dunod. 231 pp. F11.

**Mineral flotation.** W. O. BORCHERT. U. S. 1,454,838, May 8. Normally

flocculated colloidal constituents of ore pulps are dispersed and removed from the pulp in dispersed or deflocculated condition to improve the flotation properties of the remaining pulp before it is subjected to flotation. The treatment is applicable to mixed sulfide ores contg. Zn, Pb and Fe. The dispersion may be effected by Na silicate. Cf. C. A. 17, 1415.

**Flotation ore concentration.** A. C. VIVIAN. U. S. 1,449,797, Mar. 27. Taurocholic acid, cupferron, phenylglyoxime, dinitrosoresorcinol or similar organic compds. which are of weakly acid nature but amphoteric or which display pseudocacid forms are used to facilitate flotation of constituents of oxidized Sn ore, or ores of Pb, V or other oxidized mineral values. Phenolic or tarry frothing agents may be used. Cf. C. A. 17, 966.

**Metallurgical process.** W. E. F. BRADLEY. Can. 230,928, May 8, 1923. Where ores are reduced with a hydrocarbon gas the H may be removed from the molten metal and the latter carbonized by the addition thereto of a mixt. of the metal oxide and free C, the C being sufficient to reduce the metal oxide and form CO, which removes the H, and the excess C will carbonize the metal.

**Ore reduction.** J. E. LEONARZ. Can. 230,653, May 1, 1923. Heated ore is partially reduced with gas, the partially reduced ore and C are introduced into a reaction chamber over a bath of liquid metal where the reduction of the ore is completed and the metal taken into the bath. The gas from the reaction chamber is recarburetted and passed through the initial reducing chamber and part of it is returned to the reaction chamber.

**Reduction of metallic oxides.** J. E. LEONARZ. Can. 230,654, May 1, 1923. Ore is partially reduced by intimate contact with reducing gas, the ore is mixed with C and delivered to a bath of molten metal and the gas as produced is used in the initial reduction step.

**Reduction of ores.** J. E. LEONARZ. Can. 230,650, May 1, 1923. Ores are treated with a reducing gas, the reduced metal is melted, the spent gases are drawn off and passed into contact with the molten metal in the presence of C and the gaseous product is returned for reducing the ore.

**Reducing metallic oxides.** A. E. BOURCOURD. Can. 230,805, May 8, 1923. The finely ground ore is caused to travel at regulated speed through a furnace where it is agitated to expose new surfaces to a reducing gas brought into forcible impact with the ore surfaces. App. is also specified.

**Treatment of sulfide ores, mats, etc.** F. D. S. ROBERTSON. Can. 230,596, Apr. 22, 1923. A metalliferous material contg. a sulfide, As, etc., is heated in an atm. reducing to the metal to remove substantially all the S, As, etc., in elemental form and leave the product in the metallic state.

**Recovering metallic constituents from a mixture.** G. W. MULLEN. Can. 230,585, Apr. 24, 1923. Material contg. Sn is reduced with a sulfating material such as niter cake and a reducing agent to produce  $\text{SnS}_2$  from which the Sn is recovered. Sb, Pb and Cu may be thus recovered and sepd. electrolytically or otherwise.

**Extracting zinc from its ore.** E. A. JOHANSSON and G. J. EKLUND. Can. 230,923, May 8, 1923. The ore charge is caused to slide along a spiral path in a shaft above the furnace to cause agitation and the ore is heated by the gases from the furnace.

**Smelting furnace.** A. N. JETTE. U. S. 1,454,025, May 1. The pat. involves structural features of the furnace tap hole mounting.

**Smelting furnace.** A. N. JETTE. U. S. 1,454,026, May 1. The pat. specifies a construction in which lateral skew-back plates for supporting the arch of the furnace are connected with and serve as ties between frames at opposite ends of the furnace.

**Reverberatory smelting furnace.** A. N. JETTE. U. S. 1,454,024, May 1. A secondary chamber forming a metal bay is placed at the exit of the furnace chamber and is of sufficient size to permit expansion of gases coming from the furnace. An exit flue with a damper is provided in the secondary chamber.

**Furnace for roasting ores or for destructive distillation.** J. THOMAS. U. S. 1,454,798, May 8. The furnace is mounted pivotally.

**Removing blast-furnace salamanders.** G. W. VRENNLAND and G. E. WISNER. U. S. 1,455,313, May 15. Metal forming a salamander is drained from a furnace hearth through an opening in the hearth wall formed for the purpose before the molten salamander has solidified.

**Coloring iron and steel.** WM. UTENDORFER. Can. 230,528, Apr. 24, 1923. Fe and steel articles are colored black by treating them with a moderately heated soln. composed of gallic acid, an excess of free alkali and sodium picrate.

**Refining iron or steel.** H. THOMAS. U. S. 1,453,734, May 1. The metal is fused with a flux formed of glass, lime, borax and fluorspar.

**Apparatus for drying fuel charges for shaft smelting furnaces.** E. DIRPSCHLAG. U. S. 1,455,392, May 15.

**Casting metals.** H. A. MYERS and A. D. STRAW. U. S. 1,454,064, May 8. In casting Fe or other metals, adherence between the metal and the mold is prevented by coating the mold with a metalliferous substance, *e. g.*, Zn, from which gas is formed by the heat of the cast metal.

**Mold for casting metals.** H. A. MYERS. U. S. 1,454,065, May 8. Ni and Co are used for making molds for casting ferrous metals or other metals. The mold may, *e. g.*, be formed of an alloy of Ni and Co, with or without Cu, Cr, V or Ti.

**Mold for casting metals, glass or similar materials.** H. A. MEYERS. U. S. 1,454,066, May 8. Double-walled molds adapted for casting brass, ferrous metals, or glass are filled with Pb or Zn which are maintained in molten condition, to regulate the temp. of the mold and produce uniform castings.

**Iron molds for casting metals.** H. A. MYERS and A. D. STRAW. U. S. 1,454,067, May 8. Zn is distributed over the matrix surface of an Fe mold for casting metals, in order to protect the mold.

**Containers for molten metals.** H. A. MYERS and A. D. STRAW. U. S. 1,454,068, May 8. Containers for molten metals are provided with a protective coating comprising Zn, ZnCl<sub>2</sub>, Cd, Ba or Bi together with C and Fe.

**Uniting different metals.** H. A. and W. T. SOULIS. U. S. 1,455,307, May 15. Contacting metals to be united, *e. g.*, steel and cast Fe, are joined by immersing in a metallic bath, such as an alloy of Cu, Sn and Zn, having a temp. slightly below the lowest m. p. of the metals to be joined.

**Fused salt bath for heating steel in hardening.** R. S. DEAN. U. S. 1,454,214, May 8. Fused salt baths such as those composed of BaCl<sub>2</sub> or a similar salt are maintained in a non-oxidizing condition (for heating steel) by the addition of a readily oxidizable material such as Al.

**Ductile chrome-iron sheets.** F. M. BECKET and C. E. McQUIGG. U. S. 1,454,464, May 8. Chrome-Fe sheets of relatively high ductility are prepd. by rolling or drawing the metal to sheet form and subsequently rapidly cooling the metal through the temp. range 600–400°.

**Carburizing material.** L. ABBY. U. S. 1,454,612, May 8. Carburizing briquets (for case-hardening) which are dried and shrunken are formed of charcoal mixed with lime, Na<sub>2</sub>CO<sub>3</sub> or BaCO<sub>3</sub> and tar.

**Aluminium-silicon alloys.** J. D. EDWARDS. U. S. 1,453,928, May 1. The strength and ductility of Al-Si alloys are improved by the addition of finely divided Bi or Sb 0.5–1.5% to the molten alloy, which may be formed of Al alloyed with Si 3–15%.

**Silver alloy.** A. S. HYMAN. U. S. 1,455,531, May 15. An alloy which has the appearance of Pt is formed of Ag 58.3%, Cu 16.7%, Zn 16.7% and Ni 8.3%.

**Copper alloy.** H. C. KIRK and G. H. DUMLER. U. S. 1,455,589, May 15. An alloy which can be hot-rolled and is stronger than brass is formed of Cu alloyed with Fe 10% and Ni 1%.

**Nickel alloy resistant to high temperatures.** N. L. OLSON. U. S. 1,455,651, May 15. An alloy which is adapted for making metal carbonizing boxes is formed of Fe 10–25, Cr 10–20, Ni 60–70, C 2–6, Si 1–3, Al 1–2 and Mn 1–2 parts.

**Meter vane of nickel and iron alloy.** T. D. YENSEN. U. S. 1,454,878, May 15. Meter vanes for elec. meters are formed of an alloy of about equal amts. of Fe and Ni which has a hysteresis loss of less than 1000 ergs per cc. per cycle for B = 10,000 gauss. A small amt. of Mn may be added to render the alloy readily forgible.

**Solder for aluminium.** ASAJIRO ISHIWARA. Japan. 41,184, Dec. 19, 1921. A low-melting alloy is composed of Sn 140, Al 24, Pb 12, and Sb 6 g.

**Flux for refining brass.** H. THOMAS. U. S. 1,454,361, May 8. Scrap brass is refined by fusing it with a flux formed of glass 2, borax 1 and fluorspar 1 pat.

**Ingot molds and mold feeders.** B. H. HOWARD and E. J. TURNER. U. S. 1,454,740–1–2, May 8. Structural features.

**Ingot mold.** E. GATHMANN. U. S. 1,455,197, May 15. The upper part of the ingot is chilled by a "chill top" which is removed from the mold together with the ingot itself.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROULLER AND CLARENCE J. WEST

**Electrovalency.** I. The polarity of double bonds. T. M. LOWRY. *J. Chem. Soc.* 123, 822-31(1923).—It is suggested that while a single bond may be either a covalency or an electrovalency, a double bond in org. chem. usually reacts as if it contained one covalency and one electrovalency. They are described as "mixed double bonds" and their existence can be justified on the basis of the electronic theory of valency by assigning a complete octet to each negatively charged atom and a sextet of electrons to each positively charged atom. L. states that the introduction of electrovalencies into org. chemistry provides a uniform interpretation of unsatn., reactivity, especially in compds. such as  $\text{Me}_2\text{Zn}$  and  $\text{RMgX}$ , partial valencies, conjugation, alternate polarities, crossed polarities in conjugated systems, structure of  $\text{C}_6\text{H}_6$ , the laws of substitution in  $\text{C}_6\text{H}_6$ , crossed polarities in  $\text{C}_6\text{H}_6$ , structure of  $\text{C}_{10}\text{H}_8$ , etc., crystal structure of graphite, structure of  $\text{CO}_2\text{H}$  acids, etc., coordination, tautomeric or bipolar ions, and the relation between tautomerism and coordination. All the previous attempts to represent electrovalencies can now be replaced by the  $\approx$  sign, which is used universally to represent electrovalency in compds. such as  $\text{NaCl}$ .

C. J. WEST

**Preparation and examination of methylpentene,  $(\text{CH}_3)_2\text{C}:\text{CHC}_2\text{H}_5$ .** H. VAN RIJSSEGHEM. *Bull. soc. chim. Belg.* 32, 144-50(1923).—Methylpentene is prepd. by dehydration with *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$  of dimethyl propylcarbinol, which is obtained: 1. from  $\text{MeCOPr}$  and  $\text{MeMgI}$  (this ketone being prepd. by passing a mixt. of  $\text{AcOH}$  and  $\text{PrCO}_2\text{H}$  over  $\text{ThO}_2$ ); 2. from  $\text{PrCO}_2\text{Me}$  and  $\text{MeMgI}$  according to the method of Masson (*Compt. rend.* 132, 484). By both methods is obtained a mixt. of hydrocarbons b. about  $60-70^\circ$ . With the second method the larger part of the product b.  $66.7-7.2^\circ$ . All fractions were examd. as to their  $\text{Br}_2$ -adding capacity and were found to contain one double bond per mol.; they are likely, therefore, to be isomers or homologs. The  $66.7-7.1^\circ$  fraction (21 g.) oxidized with  $\text{CrO}_3\text{-AcOH}$  gave 2.5 g.  $\text{EtCHO}$ , 10 g.  $\text{EtCO}_2\text{H}$  and 10 g. acetone, proving that this fraction is pure  $\text{Me}_2\text{C}:\text{CHEt}$ , having a f. p.  $-134.75^\circ$ ,  $d_4^{15}$  0.69145,  $n_D^{20}$  1.4003,  $n_D$  1.4028, viscosity  $\eta_s$  0.00373. Satg. the  $\text{Me}_2\text{C}:\text{CHEt}$  with  $\text{Br}_2$  gives the dibromide, f. p. approx.  $-49^\circ$  to  $-54^\circ$ ,  $d_4^{15}$  1.5825,  $n_D^{20}$  1.50294,  $n_D$  1.506225,  $n_D$  0.03530,  $\text{Cl}_2$  and  $\text{Me}_2\text{C}:\text{CHEt}$  give a compd.  $\text{C}_6\text{H}_{10}\text{Cl}_2$ , b.  $34-6^\circ$ , and another compd. contg. more Cl than  $\text{C}_6\text{H}_{10}\text{Cl}_2$ , b.  $82-4^\circ$ .

R. BRUTNER

**Spinacene: its oxidation and decomposition.** A. C. CHAPMAN. *J. Chem. Soc.* 123, 769-79(1923); cf. *C. A.* 12, 1766.—The following additional phys. properties are recorded:  $d_4^{20}$  0.8588,  $n_D^{20}$  1.4951, sp. refraction, 0.3396, mol. refraction, 134.5, heat of combustion, 4,388 and 4,372 (2 expts.). The hydrogenated hydrocarbon, spinacene,  $\text{C}_{20}\text{H}_{30}$ , b.  $280-1^\circ$ ,  $d_4^{15}$  0.8144,  $d_4^{20}$  0.8119,  $n_D^{20}$  1.4532, heat of combustion, 4,540. The dodecylbromide has again been prepd. and the purified product agrees with the formula  $\text{C}_{20}\text{H}_{34}\text{Br}$ . Spinacene can be dissolved in a mixt. of equal parts of concd.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  without any apparent decompn. provided the temp. is kept low. The action of 100%  $\text{H}_2\text{O}_2$  in glacial  $\text{AcOH}$  upon spinacene gave a compd.,  $\text{C}_{27}\text{H}_{48}\text{O}_8$ , resinous, softens  $40^\circ$  (decompn.), shows only slight peroxide properties, is readily further oxidized by 1%  $\text{KMnO}_4$  giving a compd.,  $\text{C}_{28}\text{H}_{48}\text{O}_7$ , granular, with acidic properties. Decompn. of spinacene by heating at 45 mm. and causing the vapors to pass over heated Pt (dull red heat) gave a hydrocarbon, heparene,  $\text{C}_{10}\text{H}_{18}$ , b.  $79-83^\circ$ ,  $n_D^{20}$  1.4606,  $n_D$  1.4584. *Br deriv.*,  $\text{C}_{10}\text{H}_{18}\text{Br}$ , m.  $136^\circ$ . The low boiling fraction of the decompn. products contained 1 or more of the aenylenes with some  $\text{C}_2\text{H}_4$  (isoprene?). The gaseous fraction contained about 75% unsatd. and 25% satd. hydrocarbons. The constitution of spinacene is provisionally represented as  $\text{CH}_3(\text{CH}:\text{CMe}:\text{CH}:\text{CHCHMeCH}_2\text{CH}_2\text{CMe}:\text{CHET})_2$ .

C. J. WEST

**Preparation of absolute alcohol with calcium chloride and lime.** W. A. NOYES. *J. Am. Chem. Soc.* 45, 857-62(1923).—From strong alc. contg. somewhat more than 1 mol.  $\text{CaCl}_2$  for 1 mol.  $\text{H}_2\text{O}$ , alc. of 99.5% concn. or stronger may be distd. On concn. of such a soln. a solid alcoholate, not a hydrate, begins to sep. when the b. p. reaches  $95-100^\circ$  and there is an equil. between the alcoholate and hydrate present. A rather high temp. is required to expel the alc. from the solid alcoholate. The hydrate of  $\text{CaCl}_2$  with 4.5 mols.  $\text{H}_2\text{O}$  b.  $140^\circ$  and from such a soln. the alc. may be distd. completely with a concn. of 90% or greater. Ten successive distns. of alc. contg. 80 g.  $\text{CaCl}_2$  per l. increase its concn. from 83% to 99.50%. An app. is described by means of which 99.0-9.5% alc. can readily be prepd. with  $\text{CaCl}_2$  with practically no loss of alc. An

app. is also described for prep. abs. alc. (99.9% or stronger) with lime. When abs. alc. is distd. from an excess of lime, a little Ca passes over, probably as  $\text{Ca}(\text{OEt})_2$ . Metallic Na is not suitable for the prep. of abs. alc.

**Purification and some physical properties of certain aliphatic alcohols.** II. R. F. BRUNEL. *J. Am. Chem. Soc.* **45**, 1334-8 (1923); cf. *C. A.* **15**, 1530.—The thermo-element used in the earlier work has been recalibrated and the temps. were followed during the distn. and not, as before, in the b. p. app. subsequent to the distn.  $\text{PrOH}$  was purified through the H phthalate, m.  $54-5^\circ$ ; the other alcs. were prepd. by reduction of the purified ketones. Below are given, resp., the b. p. (pressure in parentheses),  $d_4^{25}$  and  $n_D^{25}$  (the error in d. should not exceed 0.0001 except in the case of  $\text{Pr}_2\text{CHOH}$ ; that in  $n$  is probably 0.0001):  $\text{Me}_2\text{CO}$   $56.085 \pm 0.01^\circ$  (760), . . . . .;  $\text{MeCOEt}$   $79.370 \pm 0.01^\circ$  (755) . . . . .;  $\text{PrOH}$   $97.175 \pm 0.01^\circ$  (760), 0.7998, 1.3834;  $\text{Me}_2\text{CHOH}$   $82.258 \pm 0.005^\circ$  (760), 0.7808, 1.3748;  $\text{MeEtCHOH}$   $99.529 \pm 0.005^\circ$  (760), 0.8023, 1.39495;  $\text{MePrCHOH}$   $119.275 \pm 0.01^\circ$  (754), 0.80483, 1.4043;  $\text{Et}_2\text{CHOH}$   $115.40 \pm 0.01^\circ$  (754), 0.8154, 1.4077;  $\text{Me}(\text{Me}_2\text{CHCH}_2)\text{CHOH}$   $131.85 \pm 0.01^\circ$  (760), 0.80245, 1.40895;  $\text{Pr}_2\text{CHOH}$   $155.00 \pm 0.04^\circ$  (750), 0.8129, 1.4178.

**Preparation of the ethers of primary alcohols.** JEAN POPELIER. *Bull. soc. chim. Belg.* **32**, 179-94 (1923).—The formation of  $\text{Et}_2\text{O}$  from  $\text{EtOH}$  by means of  $\text{H}_2\text{SO}_4$  can be run as a continuous process owing to the lower b. p. of  $\text{Et}_2\text{O}$ . With the higher homologs—Am and Bu alc.—the ethers have a higher b. p. than the resp. alcs. P., at first studied with iso-AmOH the conditions under which the optimum output of ether is obtained, varying the amt. of  $\text{H}_2\text{SO}_4$ , the temp., and the duration of the distn. The velocity of the etherification is proportional to the amt. of  $\text{H}_2\text{SO}_4$ ; the formation of amylene—a secondary reaction—is accelerated by an increase of temp. and by the higher concn. of ether accumulating in the vessel at the end of the reaction. The best results are obtained with 10 or 15%  $\text{H}_2\text{SO}_4$  at  $125-40^\circ$ , the velocity of the distn. being 10-15, or 20-25 drops per min. Most of the iso-AmOH is contained in the distillate; the residue contg. the ether +  $\text{H}_2\text{SO}_4$  is distd. with steam. The ether, thus obtained, is rectified. (iso-Am) $_2\text{SO}$ , present in the residue of the steam distn., is distd. under 12 mm.; it b.  $139-41^\circ$ , f. p.  $20^\circ$ .  $\text{Bu}_2\text{O}$ , obtained in the same way from  $\text{BuOH}$ ,  $n_D^{15}$  1.4010, b.  $141.9^\circ$ ,  $d_4^{15}$  0.7725;  $\text{Am}_2\text{O}$ , prepd. in the same way from  $\text{AmOH}$ ,  $n_D^{15}$  1.4116, b.  $187.9^\circ$ ,  $d_4^{15}$  0.7864. With iso-BuOH the etherification was found to be impossible as the temp. required for the reaction could not be attained owing to the low b. p. of the alc. ( $108^\circ$ ). A mixt. of iso- and  $n$ -BuOH was, therefore, etherified, giving 40%  $\text{Bu}_2\text{O}$ , 57% mixed ether (iso-BuOHu) and 3% (iso-Bu) $_2\text{O}$ , which confirms the assumption that the etherification of iso-BuOH is slower than that of the other alcs. The b. p. of  $\text{Pr}_2\text{O}$  ( $90.5-1.5^\circ$ ) is lower than that of  $\text{PrOH}$  ( $97-7.8^\circ$ ); the etherification is, therefore, similar to that of  $\text{EtOH}$ . The quantity of  $\text{H}_2\text{SO}_4$  must not be too large in this case, in order to prevent the formation of amylene which is readily formed. With 11%  $\text{H}_2\text{SO}_4$ , 57.7% of the alc. is transformed into the ether,  $d_4^{15}$  0.7505.

R. BEUTNER

**The existence of alkyl chlorites.** G. R. LEVI. *Gazz. chim. ital.* **53**, 40-2 (1923).—In connection with other work on chlorites (Bruni and Levi, *C. A.* **10**, 1620; **16**, 2474; 3789). L. attempted to prep. alkyl chlorites.  $\text{MeClO}$  and  $\text{EtClO}$  are known, but esters of  $\text{HClO}_2$  and  $\text{HClO}$  are not known. Preliminary tests with  $\text{MeI}$  or  $\text{EtI}$  with  $\text{AgClO}_2$  exploded with flame at once, thus demonstrating the need of a solvent. Dry  $\text{Et}_2\text{O}$  and abs.  $\text{EtOH}$  were best suited. Since  $\text{AgClO}_2$  could not safely be pulverized a suitable powder was obtained by pptg.  $\text{AgClO}_2$  from a soln. of  $\text{NaClO}_2$  with  $\text{AgNO}_3$ . 10 g.  $\text{AgClO}_2$  in 20 cc. abs.  $\text{EtOH}$  were mixed with 7.5 g.  $\text{EtI}$  in an equal vol.  $\text{EtOH}$  at  $15^\circ$ . No visible change occurred until the temp. was allowed to rise slowly, when the yellow  $\text{AgClO}_2$  became lighter in color due to  $\text{AgI}$ . Presently the soln., as well as the unchanged  $\text{AgClO}_2$ , exploded. Other unsuccessful attempts are described. L. believes that the alkyl esters should be stable and knows that  $\text{AgClO}_2$  is stable under the conditions used. Further attempts are to be made.

E. J. WITZEMANN

**Action of the organo-magnesium salts upon sulfonyl chloride.** Preparation of the aliphatic sulfonyl chlorides and bromides. E. CHERBULIEZ AND O. SCHNAUDER. *Helvetica Chim. Acta* **6**, 249-57 (1923).—The action of the organo-Mg salts upon  $\text{SO}_2\text{Cl}_2$  gives rise to sulfonyl chlorides together with sulfonic acids (Oddo, *Atti Accad. Lincei* [5] **14**, I, 189 (1905); *Gazz. chim. ital.* **35**, II, 136 (1905)). The formation of these two classes of compds. may be explained by assuming the formation of an intermediate

complex of the type:  $\text{X} \xrightarrow{\text{R}} \text{Mg} \begin{array}{l} \text{SO}_2 \\ \text{Cl} \end{array}$  (where X is a halogen), which may break up into either  $\text{RSO}_2\text{X}$  or  $\text{RSO}_2\text{Cl}$ . The aliphatic sulfonyl chlorides were prepd. in 25-35%



yield by adding at 10° 0.1 g. mol. of the organo-Mg compd. in 50 cc. Et<sub>2</sub>O to 35 g. SO<sub>2</sub>Cl<sub>2</sub> in 50 cc. Et<sub>2</sub>O, and then adding ice water. The same procedure gave a very low yield of aromatic sulfonyl chlorides. Thus the Mg compd. from MeBr gave MeSO<sub>2</sub>Br, b<sub>11</sub> 72-3°; MeI gave MeSO<sub>2</sub>Cl, b<sub>17</sub> 58°; EtCl gave EtSO<sub>2</sub>Cl, b<sub>18</sub> 65°; EtBr gave EtSO<sub>2</sub>Br, b<sub>18</sub> 80°; EtI gave EtSO<sub>2</sub>Cl; PhCH<sub>2</sub>Cl gave PhCH<sub>2</sub>SO<sub>2</sub>Cl, m. 92°; PhBr gave a mixt. contg. 78% of PhSO<sub>2</sub>Br and 22% of PhSO<sub>2</sub>Cl. T. S. CARSWELL.

The action of fuming sulfuric acid on acetylene dichloride. H. LAPOUSE. *Bull. soc. chim. Belg.* 32, 139-40 (1923).—Fuming H<sub>2</sub>SO<sub>4</sub> with CHCl:CHCl gives HCl and HO<sub>2</sub>SCHClCHO, which in alk. soln. can be oxidized by air (O<sub>2</sub>) to the corresponding CO<sub>2</sub>H deriv. By hydrolysis (with 60% H<sub>2</sub>SO<sub>4</sub>) are obtained H<sub>2</sub>SO<sub>4</sub> and CH<sub>2</sub>ClCHO. HO<sub>2</sub>SCHClCHO, which contains one asym. C atom, can be split into optical antipodes by means of strychnine. R. BEUTNER.

Reactions of chlorites with salts of hydrazine and hydroxylamine. G. R. LAVI. *Gazz. chim. ital.* 53, 105-8 (1923).—N<sub>2</sub>H<sub>4</sub>HClO<sub>2</sub> is an easily exploded compd. (Salvadori, C. A. 2, 182). In the presence of CuO, FeO or their salts chlorates, bromates and iodates oxidize N<sub>2</sub>H<sub>4</sub> to N<sub>2</sub>. With hypochlorites alk. solns. of N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O react giving N<sub>2</sub> quant. (Macbeth, C. A. 15, 3053). Preliminary expts. showed that alkali chlorites treated with com. N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O evolve N<sub>2</sub> at once, but if pure N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>O is used no N<sub>2</sub> is evolved. When the neutral salts are boiled the reaction N<sub>2</sub>H<sub>4</sub>.2HCl + NaClO<sub>2</sub> → N<sub>2</sub> + NaCl + 2H<sub>2</sub>O + 2HCl is quant. A known amt. of powdered NaH<sub>2</sub>-H<sub>2</sub>SO<sub>4</sub> suspended in a little H<sub>2</sub>O was treated with 0.5 equiv. of Ba(OH)<sub>2</sub>. The calcd. amt. (0.5 equiv.) of Ba(ClO<sub>2</sub>)<sub>2</sub> was added in portions at 0-2°. The mixt. was filtered rapidly and poured at once into EtOH at -10°, which pptd. crystals of *hydrazine chlorite* (presumably N<sub>2</sub>H<sub>4</sub>.HClO<sub>2</sub>); these were spontaneously inflammable when dry. N<sub>2</sub>H<sub>4</sub>.(HClO<sub>2</sub>)<sub>2</sub> could not be obtained as a solid. The action of NH<sub>2</sub>OH on O acids of Cl is even more energetic. The perchlorate is known but not the chlorate. Neutral solns. react thus: NH<sub>2</sub>OH.HCl + NaClO<sub>2</sub> → NaCl + Cl + NO + 2H<sub>2</sub>O but with excess NH<sub>2</sub>OH.HCl they react thus: 2NH<sub>2</sub>OH.HCl + NaClO<sub>2</sub> → NaCl + N<sub>2</sub>O + 3H<sub>2</sub>O + 2HCl. The unusual formation of N<sub>2</sub>O in such reactions is commented upon. E. J. WITZEMANN.

Magnesiylamine. GIUSEPPE ODDO AND EMANUELE CALDERARO. *Gazz. chim. ital.* 53, 64-74 (1923).—EtMgI obtained as usual in Et<sub>2</sub>O was cooled in ice and treated with dry NH<sub>3</sub>. A gelatinous gray-white ppt. of *magnesiylamine* (I), H<sub>2</sub>NMgI.OEt, was formed and C<sub>2</sub>H<sub>4</sub> was evolved. Excess NH<sub>3</sub> was removed with a current of CO<sub>2</sub>-free air. I with 2 mols. C<sub>4</sub>H<sub>9</sub>N gave the *pyridine compound* H<sub>2</sub>NMgI.2C<sub>4</sub>H<sub>9</sub>N, which is thought to be H<sub>2</sub>N.N(C<sub>2</sub>H<sub>5</sub>).N(C<sub>2</sub>H<sub>5</sub>).MgI. The evolution of C<sub>2</sub>H<sub>4</sub> is quant. for the NH<sub>3</sub> consumed in the reaction: IMgEt + NH<sub>3</sub> → IMgNH<sub>2</sub> + C<sub>2</sub>H<sub>4</sub>. After removal of the excess of NH<sub>3</sub> from a prepn. of I it was boiled 2 hrs. with BzCl. The ppt. was washed with Et<sub>2</sub>O to remove BzCl and then placed in ice H<sub>2</sub>O + AcOH, giving BzNH<sub>2</sub>, m. 128°. The reactions follow: I + BzCl → PhC(NH<sub>2</sub>)OMgI + (II); II + I → PhC(NH<sub>2</sub>)<sub>2</sub>OMgI (III) + MgICl; III + H<sub>2</sub>O → MgIOH + NH<sub>3</sub> + BzNH<sub>2</sub>. I treated similarly with BuCOCl gives BuCONH<sub>2</sub>. I boiled similarly with BzOEt, treated with Et<sub>2</sub>O and acidified with AcOH gave a ppt. composed mostly of BzNH and some BzNH<sub>2</sub>. I treated similarly with C<sub>6</sub>H<sub>5</sub>(CO<sub>2</sub>Et)<sub>2</sub> (IV) gave phthalimide thus: IV + I → (C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>)NMgI (V) + 2EtOH; V + H<sub>2</sub>O → (C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub>)NH + Mg(OH)I. I heated with PhNO<sub>2</sub> gives an addn. product, a bulky ppt., which when treated with AcOH gives PhNO<sub>2</sub> again. The C<sub>2</sub>H<sub>5</sub>N compd. of this complex, PhN(:O)NH<sub>2</sub>C<sub>2</sub>H<sub>5</sub>N, sepds. as a yellow ppt. on boiling the components 2 hrs. I heated 15 mins. with pure BzH gave a yellow powder. The last stages of this reaction follow: IMgOCHPhNHCHPhNHCHPhOMgI + 2H<sub>2</sub>O → HOCHPhNHCHPhNHCHPhOH + HOMgI - H<sub>2</sub>O → PhHC.NCHPhN:CHPh (hydrobenzamide). In the above reaction I resembles RMgI acting on -CO-derivs. But I also acts in part like NaNH<sub>2</sub>, which gives rise to Cannizzaro's reaction. The addn. product of I with Ph<sub>2</sub>CO was decompd. by H<sub>2</sub>O, giving Ph<sub>2</sub>CO. With (CH<sub>3</sub>Ac)<sub>2</sub>I readily gives dimethylpyrrole. E. J. WITZEMANN.

Action of mixed organomagnesium compounds on ethylglycerol epibromohydrin. RAYMOND DELABY. *Compt. rend.* 176, 1153-6 (1923).—By the action of EtMgBr upon ethylglycerol epibromohydrin (I) 1,3-dibromo-2-pentanol (II), b. 119.0-9.5°, was obtained. By oxidation with CrO<sub>3</sub> the 1,3-dibromo-2-pentanone (III) was formed; further oxidation gave only AcOH, thus differing from the 1,2-dibromo-3-pentanol, which gives AcOH and EtCO<sub>2</sub>H. From III a bromoketonetriazine, m. 115-7°, was obtained. PhMgBr reacts with I to form II together with a monobromohydrin, which gave with Et<sub>2</sub>NH a diethylaminophenylpentanol, b<sub>11</sub> 150-5°. T. S. CARSWELL.

Stability of sodium formate, acetate, and oxalate towards oxidation under pressure.

HANS SCHRADER. *Ges. Abh. Kenntnis Kohle* 5, 193-9(1920).—At 160°, no oxidation of these salts takes place in 8 hours. Oxidation takes place freely at 210° and rapidly at 260°. Na formate and Na oxalate are oxidized equally quickly, while NaOAc is more slowly attacked. The presence of Na<sub>2</sub>CO<sub>3</sub> or NaOH has no marked effect. Intermediate stages between the 8 org. acids and CO<sub>2</sub> were not observed. No oxalate was formed from formate, neither was oxalate or formate formed from acetate. J. C. S.

Binary systems between ( $\alpha$ - and  $\beta$ -)monochloroacetic acid and phenols. IV. F. FISIO MAMMELI AND GLAUCO COCCONI. *Gazz. chim. ital.* 53, 149-58(1923).—In continuing earlier work (*C. A.* 7, 1882, 3761; 8, 1755) M. and C. have examd. other equil. systems. contg. a polymorphic and a nonpolymorphic compd. The systems used contained 1 of the 2 forms  $\alpha$ - or  $\beta$ -CH<sub>2</sub>ClCO<sub>2</sub>H and phenols (for the component cyclic OH compds. belonging to the same series), which give addn. products (oxonium salts) with strong acids but not with weak acids like AcOH. CH<sub>2</sub>ClCO<sub>2</sub>H is an acid of intermediate strength. In the fusion diagrams of CH<sub>2</sub>ClCO<sub>2</sub>H with PhOH, cresol, etc. it has previously failed to form addn. products with these compds., but only the stable  $\alpha$ -form (m. 61.8°) was used. M. and C. have now also studied the behavior of the less stable  $\beta$ -form (m. 56.6°). 16 systems with  $\alpha$ - and  $\beta$ -CH<sub>2</sub>ClCO<sub>2</sub>H, resp., and PhOH, *o*-, *m*-, *p*-cresol,  $\alpha$ - and  $\beta$ -thymol and guaiacol were studied. In no case was the formation of an addn. compd. observed. Both forms of CH<sub>2</sub>ClCO<sub>2</sub>H behave like acid of medium strength toward all of the phenols examd. For the present this is attributed, in agreement with Kendall (*C. A.* 10, 2096), to the relatively small difference in the dissociation consts. of the 2 components of the systems. For numerical data and graphs for the f. p. curves of these systems see the original.

E. J. WITZEMANN

The constitution of eleomargaric acid. A. VERCRUYSE. *Bull. soc. chim. Belg.* 32, 151-6(1923).—Eleomargaric acid is known to contain 2 double bonds—adding Br 4 atoms—and 18 C atoms—yielding stearic acid by hydrogenation. By oxidation with alk. KMnO<sub>4</sub> (103 g. KMnO<sub>4</sub> for 30 g. of the fatty acid) V. obtained *valeric acid*, identified as its Ag salt, and *azelaic acid*, identified by its m. p. and analysis. In this oxidation the larger part is oxidized to CO<sub>2</sub>. The quantity of CO<sub>2</sub> formed agrees with the amt. calcd. By oxidizing with O<sub>3</sub> in CHCl<sub>3</sub> for 10 days, 50% valeric, 75% azelaic acid, and 9% succinic acid are obtained. V. concludes that eleomargaric acid has the structure Me(CH<sub>2</sub>)<sub>2</sub>CH:CH(CH<sub>2</sub>)<sub>2</sub>CH:CH(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H.

R. BRUTNER

The highly unsaturated fatty acids of fish oils. J. B. BROWN WITH G. D. BRAL. *J. Am. Chem. Soc.* 45, 1289-303(1923).—The name "clupanodonic acid" is retained for the acid C<sub>21</sub>H<sub>32</sub>O<sub>2</sub> (I) to which it was originally assigned by Tsujimoto, although the latter has since given it to the compound C<sub>22</sub>H<sub>34</sub>O<sub>2</sub> (*C. A.* 15, 1227; 16, 3548). The Me, Et and Bu esters of the acids of menhaden oil were prepd. by refluxing in the alc. with HCl and brominated in Et<sub>2</sub>O at -10° to -5°. The Br content of the polybromides indicates the presence of acids more highly unsatd. than I. Similar treatment of linseed acids gave *Bu hexabromostearate*, si- ters 157°, m. 160°. While the free fatty acids of menhaden oil slowly polymerize on heating to 240° in CO<sub>2</sub>, the esters do not and may be distd. almost to dryness *in vacuo*. Analysis of the Me esters from 5 fish oils in the same way likewise indicated the presence of acids more highly unsatd. than I. By fractionating the Me esters of menhaden oil 6 times *in vacuo*, B. and B. obtained indications of the presence of acids with 16, 18, 20 and 22 C atoms. The unsatd. acids obtained by the Pb soap-Et<sub>2</sub>O and the Ba soap-C<sub>6</sub>H<sub>6</sub> methods of sepn. were esterified and fractionated and the Br addn. products analyzed. The Et<sub>2</sub>O-insol. Br addn. products were debrominated with Zn dust in MeOH, BuOH and PhCH<sub>2</sub>OH and fractionated and their Br addn. products analyzed. B. and B. believe their results demonstrate the presence in fish oils of myristic, palmitic, palmitoleic (hexadecatrienoic), clupanodonic (octodecatetrenoic), arachidonic, eicosapentenoic, docosapentenoic and docosahexenoic acids. In the course of the work were obtained *Me ocolobromostearate*, amorphous, m. 240°, and *Me clupanodonate*, b<sub>14</sub> 215°, n<sub>20</sub> 1.4860, I no. (Wijs) 348.8; it is believed that this is the first instance where any deriv. of I has ever been obtained in reasonably pure state.

C. A. R.

The rate of reaction between ethylene and bromine. T. D. STEWART AND K. R. EDLUND. *J. Am. Chem. Soc.* 45, 1014-24(1923).—The reaction between gaseous C<sub>2</sub>H<sub>4</sub> and Br did. with air takes place for the most part, if not entirely, on the walls of the contg. vessel. No evidence of a gaseous reaction was found. The reaction rate is increased by the presence of H<sub>2</sub>O. With a const. surface the rate is proportional to the concn. of both the C<sub>2</sub>H<sub>4</sub> and the Br. No evidence of a deviation from a bimol. reaction was found. The specific reaction rate during the first 12 sec. is apparently greater than the subsequent rate but the abnormality does not involve more than 1% of the C<sub>2</sub>H<sub>4</sub>. This small initial reaction probably owes its higher velocity to wall catal-

ysis and is not to be taken as evidence of a highly reactive form of  $C_2H_4$  present in small amt. C. A. R.

**Action of bromine upon hydrocarbons.** B. K. MERESHKOWSKY. *Ann.* 431, 113-32 (1923).—The ratio of reaction products obtained in bromination of hydrocarbons or their Br derivs., by using pure Br, Fe wire,  $FeBr_3$  and Al or  $AlCl_3$  was found to be:  $CH_2BrCHBrCH_2Br$  and  $MeCHBrCHBr_2$ : 100, —; 70, 30; 20, 80; 50, 50.  $CH_2BrCMeBrCHBr_2$  and  $Me_2CBrCHBr_2$ : 100, —; 100, —; 30, 70; 30, 70;  $CH_2BrCBr(CH_2Br)_2$  and  $CH_2BrCMeBrCHBr_2$ : 50, 50; 30, 70; 10, 90; 15, 85. The following rules are proposed: If the mol. contains  $n$  C atoms,  $n-1$  atoms of halogen will enter the mol., whether or not a catalyzer is used, at temps.  $<100^\circ$  and will be attached to those C atoms in which substitution has not yet taken place. If  $n-1$  C atoms have a halogen atom attached to them, an additional atom of halogen will in part attack the halogen-free C atom, in part that substituted C atom which carries the largest no. of H atoms. Further substitution in general concerns the C atom which possesses the greatest no. of H atoms. In all cases the substitution process proceeds in several directions, which in part depends upon the chem. character of the catalyzer. Br and  $MeCH:CH_2$  give a 90% yield of  $MeCHBrCH_2Br$  (I) and 4%  $CH_2BrCHBrCH_2Br$  (II),  $b_p$  103-4°. Distd. at the ordinary pressure, the latter splits off HBr, yielding  $CH_2:CHCH_2Br$  (*Ann.* 154, 371; 156, 168),  $b_{140}$  140.5-1.5°,  $d_4^{20}$  1.9702,  $d_4^{20}$  1.9336;  $n_{20}:\alpha$ , 1.51250; D, 1.51566;  $\beta$ , 1.52464;  $\gamma$ , 1.53182. I and Br with Fe wire as catalyzer gave II and  $MeCHBrCHBr_2$ ,  $b_p$  88-90°,  $d_4^{20}$  2.39984;  $d_4^{20}$  2.36102;  $n_{20}:\alpha$ , 1.57072; D, 1.57451;  $\beta$ , 1.58531;  $\gamma$ , 1.59432. The unsatd. bromide,  $C_4H_4Br_2$  (*Ann.* 136, 155), obtained by the action of AcOH and AcOK,  $b_{159}$  128-30°,  $d_4^{20}$  2.04389,  $d_4^{20}$  2.00537;  $n_{20}:\alpha$ , 1.52643; D, 1.53042;  $\beta$ , 1.54026;  $\gamma$ , 1.54958. The action of pure Br upon  $Me_2C:CH_2$  at 45-50° gave 3%  $C_4H_4Br$ , 45%  $C_4H_4Br_2$ , 44%  $C_4H_4Br_3$ , 7%  $C_4H_4Br_4$  and 1%  $C_4H_4Br_5$  and  $C_4H_4Br_6$ .  $(CH_2Br)_2CMeBr$ , m. -32° and  $b_p$  222-5° (some decompn.). Fe as a catalyzer gave only the tribr mide (1,2,3), while  $FeBr_3$  gave a mixt. of the 1,2,3- and the 1,1,2-derivs.  $CH_2BrCMeBrCHBr_2$ ,  $b_{15}$  134-5°,  $d_4^{20}$  2.48766,  $d_4^{20}$  2.45445;  $n_{20}:\alpha$ , 1.59484; D, 1.599902;  $\beta$ , 1.61187;  $\gamma$ , 1.62239. The acetate,  $Br_2C:CMeCH_2O_2CMe$ , obtained by heating with AcOH and AcOK,  $b_{15}$  114°,  $d_4^{20}$  1.77913,  $d_4^{20}$  1.75070;  $n_{20}:\alpha$ , 1.51425; D, 1.518477;  $\beta$ , 1.52789;  $\gamma$ , 1.53553.  $(CH_2Br)_2CBrCH_2Br$ ,  $b_{14}$  150-1°,  $d_4^{20}$  2.59568,  $d_4^{20}$  2.55953;  $n_{20}:\alpha$ , 1.62014; D, 1.62462;  $\beta$ , 1.63590;  $\gamma$ , 1.65048. The acetate,  $CHBr:C(CH_2OAc)_2$ ,  $b_{14}$  136°,  $d_4^{20}$  1.47595,  $d_4^{20}$  1.45335;  $n_{20}:\alpha$ , 1.48195; D, 1.48525;  $\beta$ , 1.439228;  $\gamma$ , 1.50006. The glycol,  $CHBr:C(CH_2OH)_2$ ,  $b_{12}$  152.2°,  $d_4^{20}$  2.71775;  $d_4^{20}$  1.69582;  $n_{20}:\alpha$ , 1.53670; D, 1.540544;  $\beta$ , 1.550465;  $\gamma$ , 1.55846. It solidifies at -80°. A small amt. of a compd.,  $C_4H_4Br_4$ , m. 93° was also isolated. C. J. WEST

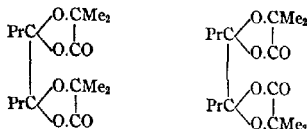
Some derivatives of the glycerol  $CH_2(OH)CH(OH)C:CCH_2OH$ . M. LÉSPIRAU. *Compt. rend.* 176, 1068-70 (1923).—The oxide  $O.CH_2.CHC:CCH_2OMe$ ,  $b_{15}$  75-6°,

$d_{25}$  1.024,  $n_D$  1.4573, was prepd. by the action of  $ClCH_2CHO$  on the mixed Mg deriv. of  $HC:CCH_2OMe$  (*C. A.* 3, 1164). The chlorohydrin (I),  $CH_2ClCH(OH)C:CCH_2OMe$ , obtained by the action of HCl upon the oxide,  $b_{12}$  119-20°,  $d_{25}$  1.0508,  $n_D$  1.4608. The action of  $MeONa$  on I forms the ether  $MeOCH_2CH(OH)C:CCH_2OMe$ ,  $b_{12}$  119-20°,  $d_{25}$  1.0508,  $n_D$  1.4608. The glycol-ether  $CH_2(OH)CH(OH)C:CCH_2OMe$ ,  $b_{12}$  155-6°,  $d_{25}$  1.1274,  $n_D$  1.481. Its Br deriv.,  $CH_2(OH)CH(OH)CBr:CH_2OMe$ , m. 51-2°,  $b_{11}$  192°. T. S. CARSWELL

**New derivatives of diamines.** II. PETER BERGELL. *Z. physiol. Chem.* 123, 280-9 (1922); cf. *C. A.* 16, 3632.—*Dibromopropionylethylenediamine*,  $(CH_2)_2(NHCOCHBrMe)_2$ , was prepd. by adding the bromide to excess of the amine gradually and maintaining the temp. at 20°. Recrystd. from hot alc. it m. 203°. The addn. of  $N$  NaOH at intervals during the course of the reaction improves the yield. *Dichloroacetylene-ethylenediamine*,  $(CH_2)_2(NHCOCH_2Cl)_2$ , prepd. similarly, m. 171-2°. *Di- $\beta$ -naphthalenesulfonyl-ethylenediamine*,  $(CH_2)_2(NHSO_2C_{10}H_7)_2$ , was prepd. in impure condition. Attempts to replace the halogen of the above compds. by  $NH_2$  groups were unsuccessful. *Dibromopropionylidialanypentamethylenediamine*,  $(CH_2)_4(NHCOCHMeNHCOCHMeBr)_2$ , sinters 169°, m. 180°, was prepd. from dibromopropionylpentamethylenediamine by first aminizing in dil. alc. and then treating the alc.-free soln. with  $MeCHBrCOBr$ . R. L. STREHLÉ

**Synthesis of mixed  $\alpha$ -diketones by means of organo-zinc derivatives.** E. F. BLAISE. *Compt. rend.* 176, 1148-50 (1923).—By the action of  $SCl_2$  upon oxalobisoxycisobutyric acid was produced the corresponding *dichloride*,  $b_{14}$  160°, m. 76-7°. Condensation of  $PrMgI$  with the latter gave a product  $b_{14}$  165-80°, which by alcoholysis

left a cryst. mass, m. 55–80°. By repeated crystns. of the latter were obtained 2 sharply melting products, m. 72° and 82°, b<sub>11</sub> 168°, of the same compn., corresponding to the *hydroxyisobutyric bicycloacetal of dibutyl* (I). It is probable that these are stereoisomers of the forms:



Heating with HI soln. at 127° hydrolyzed I and at the same time reduced the hydrolysis product, giving PrCOBu. T. S. CARSWELL

**Dioximes.** IV. G. PONZIO. *Gazz. chim. ital.* 53, 15–19 (1923).—In the previous paper (C. A. 17, 87, 1428) it was suggested that the >NOH group in  $\alpha$ -methylbenzoylglyoxime (I), MeC(:NOH)C(:NOH)Bz has the structure :C(NO)H in order to explain the action of N<sub>2</sub>O<sub>4</sub> on I, giving MeC(:NOH)C(:N<sub>2</sub>O<sub>4</sub>)Bz, which with H<sub>2</sub>O + NH<sub>3</sub> gives MeC(:NOH)C(:NOH)NH<sub>2</sub> + BzNH<sub>2</sub>. The same formula for I [MeC(:NOH)CH(NO)Bz] permits of explaining the behavior of Ac<sub>2</sub>O and dry HCl on I, giving 3-methyl-4-nitroso-5-phenylisoxazole (II), N:CMe.C(NO).CPh.O, by the loss of H<sub>2</sub>O. The

dioximic form of I gives the di-Ac deriv. MeC(:NOAc)C(:NOAc)Bz and also methyl benzoylfuran (III), N:CMe.CBz:N.O by the loss of H<sub>2</sub>O. I when heated gives both

II and III but II appears only as a transient blue-green color. On the contrary  $\beta$ -methylbenzoylglyoxime (IV) gives with N<sub>2</sub>O<sub>4</sub> a peroxide Me(C<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)Bz and with Ac<sub>2</sub>O only the di-Ac deriv. without a trace of nitrosoisoxazole. Heated with Ac<sub>2</sub>O or fused IV gives III. With dry HCl, IV gives a little II due to a partial isomerization into I. 5 g. I were added slowly to 20 g. Ac<sub>2</sub>O + some fused NaOAc. Later the mixt. was poured into H<sub>2</sub>O and neutralized in ice with excess Na<sub>2</sub>CO<sub>3</sub>. The yellowish mass was pressed out on filter paper and extd. with Et<sub>2</sub>O, in which the di-Ac deriv. is insol. The Et<sub>2</sub>O soln. was evapd. and III removed by washing the residue with 10% NaOH. Yield 10% II. 5 g. I in Et<sub>2</sub>O treated with dry HCl in Et<sub>2</sub>O gave when treated as above a 15% yield of II, blue, m. 84°. III is formed from I by melting it, by heating it with H<sub>2</sub>O at 80–90°, by the action of Ac<sub>2</sub>O in the cold and by the action of dry HCl. III is formed from IV by melting, by boiling with Ac<sub>2</sub>O and by heating with NH<sub>4</sub>OH in the sealed tube at 160–70°. III is best obtained from I and IV by boiling with excess Ac<sub>2</sub>O + some fused NaOAc, pouring the product into H<sub>2</sub>O and distg. with steam; III seps. as white prisms, m. 42°, is quite resistant to concd. acids, and hot KMnO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub>; alkali hydroxides decomp. III into BzOH + NH<sub>3</sub>. III in EtOH with the calcd. amt. or Ph-NHNH<sub>2</sub> in glacial AcOH on the H<sub>2</sub>O bath gives the  $\alpha$ -phenylhydrazone, C<sub>6</sub>H<sub>5</sub>(ON<sub>2</sub>) of III, golden yellow, m. 101°, which, boiled with dil. HCl, gives some III and the  $\beta$ -form. With 20% NaOH, NH<sub>3</sub> is formed but most of the  $\alpha$ -form is isomerized into the  $\beta$ -form. If the  $\alpha$ -form is heated above its m. p. it is converted into the  $\beta$ -form, m. 214°, which in the sealed tube with HCl at 150° gives III. III in EtOH with *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NHNH<sub>2</sub> in 40% AcOH gives the *p*-nitrophenylhydrazone of III, yellow, m. 178–82°. While III itself is not attacked by HNO<sub>3</sub>, the  $\alpha$ - and  $\beta$ - and *p*-nitrophenylhydrazones are readily attacked. Two NO<sub>2</sub> groups are introduced. The first 2 compds. give the *dinitrophenylhydrazone*, PhC[:NNHC<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>]<sub>2</sub>C:N.O.N:CMe, yellow, m. 218°.

V. G. PONZIO AND A. PICCHETTO. *Ibid* 20–4.—Of the 2 possible dioximes of triketohydrindene, C<sub>6</sub>H<sub>4</sub>.CO.CO.CO, only the  $\alpha,\gamma$ -dioxime, C<sub>6</sub>H<sub>4</sub>.C(:NOH).CO.C:NOH

(Heusler, Schieffer, *Ber.* 32, 32(1889)), is known. The  $\alpha,\beta$ -dioxime (V), C<sub>6</sub>H<sub>4</sub>.CO.C(:NOH).C:NOH, was of special interest because of its analogy to I. V

unlike I exists in but one form, which is neither dehydrogenated nor transformed into the ketopseudonitroxime by N<sub>2</sub>O<sub>4</sub>. In time V decomp. spontaneously like true dialkyl- and diarylglyoximes in which the (C<sub>2</sub>N<sub>2</sub>O<sub>2</sub>H<sub>2</sub>) group acts like C(:NOH).C(:NOH). However, V reacts with Ni like other glyoximes (C. A. 16, 908) and gives Ac and Bz derivs. The prepn. of  $\alpha,\gamma$ -diketohydrindene, C<sub>6</sub>H<sub>4</sub>.CO.CH<sub>2</sub>.CO (Wislicenus, *Ann.*

246, 354(1888)), was improved, and its crystallographic description is given. The prepn.

of  $\beta$ -isonitroso- $\alpha,\gamma$ -diketohydrindene (VI) (W., *l. c.*) was also improved. VI does not give a Ni salt but its *Co salt* ( $C_8H_6O_2N_2Co$ ) is pptd. from  $H_2O$ -EtOH with  $Co$ -

(OAc)<sub>2</sub> and thus behaves like  $\alpha$ -BzC(:NOH)Ph, while other  $\alpha$ -oximinoketones give  $Co^{II}$  derivs. instead (C. A. 16, 2308). 10 g. VI suspended in warm EtOH and treated with 4 g.  $NH_4OH \cdot HCl + 7$  g. NaOAc in  $H_2O$  were kept at 60-70° for some time. On cooling triketohydrindene  $\alpha,\beta$ -dioxime (V), m. 168° (decompn.), sepd. V treated with  $NH_4OH \cdot HCl$  as above again gives the trioxime, white needles, m. 198° (decompn.) V is pptd. from  $NH_4OH$  with  $AgNO_3$  as the *Ag salt*,  $C_8H_6O_2N_3Ag$ . Ni is dissolved by aq. V. V in  $C_6H_5N$  with  $NiCl_2$  in EtOH treated with a few drops of  $H_2O$  seps. the *Ni salt* ( $C_8H_6O_2N_3Ni$ ), brown-yellow, browns 180°, m. 300°. Acetylating V with  $Ac_2O + NaOAc$  gives the *di-Ac deriv.*, m. 174° (decompn.). V in EtOH heated with  $PhNHNH_2$  and a little glacial AcOH gave the phenylhydrazone of V, orange-red, m. 189-90° (decompn.). VI. G. PONZIO AND L. AVOGADRO. *Ibid* 25-35.—The older work on phenylglyoxime (VII) (Ber. 24, 3497(1891) and earlier) is inaccurate. Work on VII was resumed and extended to phenylaminoglyoxime (VIII). Both VII and VIII were obtained in 2 forms of which the  $\alpha$ -form is easily isomerized into the  $\beta$ -form. The 2-forms of VII behave differently toward  $N_2O_4$ . With the  $\alpha$ -form it gives a peroxide,  $PhC:N.O.O.N:CH$ , according to Scholl (Ber. 23, 3503(1890)) and phenylfuroxan,

$\begin{array}{c} \text{CH} \cdot \text{CPh} : \text{N} \cdot \text{N} \\ \text{O} \end{array}$ , according to Wieland and Semper (C. A. 2, 1012). With the  $\beta$ -form

3 atoms H are lost, giving phenylnitroglyoxime peroxide (IX), which confirms statements in Papers II and III on the inadmissibility of the theories of Hantzsch and Werner on the constitution of VII. The  $\beta$ -forms of VII and IV give complex salts with Ni and are true dioximes that behave toward  $N_2O_4$  as though the two NOH groups are equiv. The behavior of the  $\alpha$ -form of VII and I shows, as was previously stated, that the  $\beta$ -NOH group can assume a different structure in these compds. The constitution of the compd.  $Ph(C_2N_2O_2H)$  (X) given by W. and S. will be discussed in a later paper. 50 g.  $PhCOC(:NOH)H$  in 180 cc. EtOH were heated some hrs. at 70-80°, with 24 g.  $NH_4OH \cdot HCl + 45$  g. crystd. NaOAc in 75 cc.  $H_2O$ , giving  $\alpha$ -phenylglyoxime (XI), m. 168° (decompn.), sol. in NaOH from which it is pptd. unchanged with  $CO_2$  or AcOH; in boiling dil. AcOH it gives the  $\beta$ -form. XI in  $H_2O$ -EtOH with some drops 50% AcOH and then 20%  $Ni(OAc)_2$  ppts. the bright red *Ni salt* of the  $\beta$ -form, and on cooling unchanged X also seps. XI in  $H_2O$ -EtOH with  $Ni(OAc)_2$  gives a yellow ppt. contg. 23.10% Ni;  $(C_8H_6O_2N_3Ni = 26.59\% \text{ Ni}; (C_8H_6O_2N_3)_2Ni = 15.25\% \text{ Ni})$ . XI in anhydrous  $Et_2O$  with an equimol. amt. of  $N_2O_4$  (previously distilled with  $P_2O_5$ ) gave the compd. X, m. 108°. X in  $Et_2O$  agitated with 6 N  $NH_4OH \cdot H_2O$ , dried with  $Na_2SO_4$  and evapd. gave the  $\alpha$ -form of VIII, m. 154-5° (given other names by W. and S. *l. c.*). XI in  $H_2O$ -EtOH boiled with dil. AcOH gave  $\beta$ -phenylglyoxime (XII), m. 180°. XII may be obtained by treating the mother liquors from XI in this way and pptg. XII with 20%  $Ni(OAc)_2$  as the *Ni salt*,  $(C_8H_6O_2N_3)_2Ni$ , red, m. 267° (decompn.), which when treated with dil. HCl and extd. with  $Et_2O$  gives pure XII. Aq. XII attacks Ni, Cu and Co, giving the resp. complex salts. The *Cu salt* is a coffee-colored powder with a greenish reflex, m. 181°. The *Co salt*,  $(C_8H_6O_2N_3)_2Co$ , resembles the Cu salt. 10 g. XII in dry  $Et_2O$  were treated with 10 g.  $N_2O_4$ , washed after 1 hr. with  $H_2O$ , sepd. from the  $Et_2O$  and distd. with steam. The product was washed with very dil. NaOH and crystd. from EtOH, giving IX, yellow, m. 100°. Free phenylnitroglyoxime could not be obtained because it was decompd.  $PhCOC(:NOH)Cl + NH_4OH$  gives phenylchloroglyoxime (XIII) in but one form, m. 189-90° (decompn.). Either XI or XII in  $CHCl_3$  with  $Cl_2$  also gives XIII. With  $NH_4OH$ , XIII gives VIII. XIII in  $Et_2O$  with  $Ni(OAc)_2$  in EtOH gives the *Ni salt*, red-brown, m. 167° (decompn.). With  $Ac_2O + NaOAc$ , XIII gives the *di-Ac deriv.*, m. 82°.  $\beta$ -Phenylaminoglyoxime (XIV) was obtained by boiling the  $\alpha$ -form in  $H_2O$ -EtOH with dil. AcOH, pptg. with  $Ni(OAc)_2$ , etc., as with XII. XIV, more conveniently obtained from XIII with  $NH_4OH$ , m. 195° (decompn.). XIV acts upon metallic Ni and Cu. The *Ni salt*,  $(C_8H_6O_2N_3)_2Ni$ , pptd. from solns. of XIV with  $Ni(OAc)_2$ , reddish yellow, m. 265-85° (decompn.). Concd. boiling EtOH solns. of XIV with 10%  $Cu(OAc)_2$  ppt. the *Cu salt*,  $(C_8H_6O_2N_3)_2Cu$ , bronze plates, m. 232° (decompn.). P. and A. believe that XIV is the  $\beta$ -form of VIII and a true dioxime, while the isomer of VIII that does not give a Ni salt is not.

E. J. WITZEMANN  
Preparation of sarcolactic acid. JOHN MISSENDEN. Chem. News 126, 251-2 (1923).—The hydrolysis product of intercostal tissue is carefully evapd. to a thick sirup;

while at 40° 2.5 vols. 75% EtOH are added and the whole is made up to 6 vols. with H<sub>2</sub>O. The mixt. is again evapd. to a sirup, slightly acidified (H<sub>2</sub>SO<sub>4</sub>), filtered and the sarcos-lactic acid extd. by Et<sub>2</sub>O. Muscular tissue surrounding the abdomen and femur in the human body forms a plentiful source of this acid but the regions of the lactic organs at the front of the thoracic cavity yield the best supply. C. J. WEST

**Action of the Grignard reagent on keto acids.** PHILIP K. PORTER. *J. Am. Chem. Soc.* 45, 1090-7(1923).—Isocapro lactone, b. 205-10°, was obtained in 31.5% yield from levulinic acid and 2 mols. MeMgI in Et<sub>2</sub>O, and  $\gamma$ -methyl- $\gamma$ -hydroxyhexanoic lactone, b. 76-8°, in 35.1% yield with EtMgI. C. A. R.

**Citrates of calcium and strontium.** K. P. CHATTERJEE. *J. Proc. Asiatic Soc. Bengal, Proc. 8th Indian Sci. Cong.* 17, cxxix-cxxx(1921).—Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> · 16H<sub>2</sub>O is pptd. when strong solns. of Na citrate and CaCl<sub>2</sub> are mixed. It is jelly-like, hygroscopic and readily sol. in H<sub>2</sub>O. It passes rapidly into Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> · 6H<sub>2</sub>O. Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> · 6H<sub>2</sub>O seps. in the cold with increasing rapidity up to 70°. Warmth converts it into Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> · 4H<sub>2</sub>O. Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> · 4H<sub>2</sub>O is pptd. at temps. above 70°. Its soly. decreases with temp. Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> · 1.5H<sub>2</sub>O is obtained when any Ca citrate is heated to 110°. With water it rehydrates to Ca<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> · 4H<sub>2</sub>O with evolution of heat. Analogous to the jelly-like Ca citrate, the hexahydrate, and the tetrahydrate, a jelly-like Sr citrate, a pentahydrate and a monohydrate, with similar properties, have been obtained. E. J. C.

**The physical properties of maleic, fumaric and malic acids.** J. M. WEISS AND C. R. DOWNS. *J. Am. Chem. Soc.* 45, 1003-8(1923).—Maleic anhydride (I) m. 52.6° (cor.). *dl*-Maleic acid (II) m. 128.5-9.0° in open or sealed capillaries, the m. p. of the resolidified product being lower owing to the formation of malomalic acid. Maleic acid (III) m. 130-0.5° and fumaric acid (IV) 284°. The vapor pressures of I at 72°, 100°, 130° and 160° are 6.5, 23.6, 60.0 and 180.0 mm., resp. I over 61.76 and 71.49% H<sub>2</sub>SO<sub>4</sub> at 50°, 70° and 90° changes in all cases into III, showing that the pressure of the H<sub>2</sub>O vapor is greater than the dissociation pressure of III. Solubilities (in 100 parts solvent): III and IV, resp.: H<sub>2</sub>O, 25°, 78.8, 0.70; 40°, 112.5, 1.07; 60°, 148.7, 2.4; 97.5°, 392.6, —; 100°, —, 9.8; 95% alc., 29.7°, 69.9, 5.75; Et<sub>2</sub>O, 25°, 8.19, 0.72; CHCl<sub>3</sub>, 25°, 0.011, 0.02; CCl<sub>4</sub>, 25°, 0.002, 0.027; C<sub>6</sub>H<sub>6</sub>, 25°, 0.024, 0.003; Me<sub>2</sub>CO, 29.7°, 35.77, 1.72; xylene, 29.7°, 0.0085, 0.037; coal tar heavy solvent, 29.7°, 0.0085, 0.0343. II in H<sub>2</sub>O: 26°, 144.8; 50°, 222.0; 60°, 268.4; 70°, 332.0; 79°, 411.5. I (g. in 100 cc. satd. soln. at 29.7°): xylene, 16.32; coal tar heavy solvent, 9.04.  $d_4^{25}$  of solns. of II and III is shown graphically. Comparative expts. on the gain in wt. of II, tartaric and citric acids over 43.7 and 10% H<sub>2</sub>SO<sub>4</sub> indicate that pure II has somewhat less tendency than the other 2 acids to absorb H<sub>2</sub>O under extreme atm. conditions and that under normal atm. conditions there is little likelihood of trouble from the absorption of H<sub>2</sub>O from the air by II in storage. C. A. R.

**A revision of Rosanoff's diagram of the aldose sugars.** J. J. WILLAMAN AND CLARENCE A. MORROW. *J. Am. Chem. Soc.* 45, 1273-80(1923).—R.'s diagram has been modified to make it include all the known sugars and to include more facts about these sugars. Diagrams have also been constructed for the known ketoses and for the methyl-aldoses. C. A. R.

**Some constitutional problems of carbohydrate chemistry.** J. C. IRVINE. *J. Chem. Soc.* 123, 898-921(1923).—A lecture dealing with structural studies of the simple and complex carbohydrates. C. J. WEST

**Humic acids.** IV. Preparation and properties of artificial and natural humic acids. WILHELM ELLER. *Ann.* 431, 133-61(1923); cf. C. A. 16, 2315.—Humic acids are dark brown, amorphous substances, which do not melt but split off H<sub>2</sub>O and CO<sub>2</sub> at about 80°. Three classes are recognized: natural, those formed from sugars and those from phenols. Of the last several sub-classes may be distinguished. While the elementary compn. is not a criterion of the classes, it does show a certain difference, especially in the H content: Natural: C 59.6-60.2, H, 3.2-3.4; hydroquinol, pyrocatechol, hydroxyhydroquinol, its triacetate and quinone: 58.06, 3.26; pyrogallol, hexahydroxydiphenyl, purpurogallin, 56.49, 2.44; salicylic acid, hydroquinolcarboxylic acid, 2,2,2',4'-tetrahydroxydiphenyl, 57.25, 3.02; PhOH, *o*-MeC<sub>6</sub>H<sub>4</sub>OH, resorcinol and 3,5,3',5'-tetrahydroxydiphenyl, 59.0-61.9, 2.8-3.5; carbohydrates, 60.42, 5.07. The natural and the acids prepd. from phenols agree in all their properties (soly., autoxidation, behavior with PhNHN:C(NH<sub>2</sub>)<sub>2</sub>). The acids from carbohydrates show enough deviation in their reactions to be considered a sep. group. The acids were obtained from sugars (cane sugar, grape sugar, milk sugar) by the action of 75% H<sub>2</sub>SO<sub>4</sub> upon a soln. of 100 g. sugar in 100 cc. H<sub>2</sub>O. That from cellulose had a C content of 64.89. The acids from phenols were prepd. by oxidation in alk. soln. with atm. O,

$K_2S_2O_8$  or  $H_2O_2$  and in some cases by anodic oxidation. These are sol. in alkali with a deep brown color and are pptd. unchanged by acids. In  $H_2O$  or  $EtOH$  the moist acids form colloidal solns., which are flocculated by many electrolytes; the  $EtOH$  soln. is pptd. by addn. of  $Et_2O$ . Soly. in  $PhOH$ ,  $AcMe$ ,  $AcOH$  or  $MeOH$  appears to depend upon the state of division of the acids.  $HNO_3$  dissolves the acids, giving red-brown solns., from which  $H_2O$  ppts. red-brown flakes.  $Cl$  gas gives a yellow,  $Br$  a brown product. The acids are decompd. by  $Br-KOH$ , giving  $CHBr_3$  and  $CBr_4$ . Alk.  $KMnO_4$  is decolorized. Warming at  $100^\circ$  with  $PhNHN:C(NH_2)_2$  liberated  $N$  from the latter substance.  $H_2O$  is adsorbed from the air. The greatest adsorptive power is manifested towards  $NH_3$ . Natural humic acids show the same properties. V. Action of nitric acid upon humic acids. W. ELLER, HARRY MEYER and HANS SAENGER. *Ibid* 162-77.— $HNO_3$  (d. 1.4) and humic acid from hydroquinol at  $30-40^\circ$  (not over  $70^\circ$ ) give 8-32% of seminitrohumic acid,  $(C_{12}H_7O_6.NO_2)_x$ , brown-red amorphous powder purified by pptn. from  $EtOH$  by  $Et_2O$ , very hygroscopic and with a tendency to form colloidal systems. While the aq. soln. reacts acid, it does not decomp.  $K_2CO_3$ .  $NH_3$  is not split off by heating with  $KOH$ . Warming with  $KCN$  develops a deep red color. Alk.  $KMnO_4$  is not decolorized;  $PhNHN:C(NH_2)_2$  is decompd. with evolution of  $N$ . A reduction product could not be obtained. Distn. with  $Zn$  dust gave an oil, with a quinine-like odor while  $Hl$  and red  $P$  gave an oil with a  $C_{10}H_8$ -like odor. If boiling  $HNO_3$  is used, hydroxynitrohumic acid, yellow, amorphous, hygroscopic powder with acid taste, results. It differs from the semi-acid by its insoly. in  $EtOH$ . Natural humic acid behaves similarly. Among the oxidation products of humic acid by  $HNO_3$  are  $(CO_2H)_2$ ,  $CO_2$  and  $HCN$ ; indications of a  $PhNO_2$  deriv. were obtained, though no such compd. could be isolated. Addn. of benzoquinone to  $HNO_3$  at  $100^\circ$  gives a nitroquinonehumic acid, brown-yellow, amorphous, hygroscopic powder of acid taste; heating with  $KOH$  splits off small amts. of  $NH_3$ .  $HNO_3$  with carbohydrate-humic acid gives the compd.  $(C_{12}H_{11}O_{14}N_2)_x$ , a light yellowish brown, amorphous powder, with a bitter taste, which is reactive towards light when moist, but is more stable when dried. Neutral  $KMnO_4$  is decolorized by the solid powder. Colloidal aq. solns. are flocculated by many electrolytes. VI. Action of chlorine upon humic acid. W. ELLER, E. H. EROFF and H. SAENGER. *Ibid* 177-86.—Chlorohumic acid,  $C_{10}H_5O_6Cl_3$ , obtained from  $Cl$  and an aq. suspension of humic acid from hydroquinol at  $50-70^\circ$ , light and air being excluded, it is a golden yellow, amorphous powder, slowly decompd. at  $100^\circ$ . An aq. suspension at  $80-90^\circ$  evolves  $CO_2$ ; excess alkali completely decomp. the deriv.,  $CHCl_3$  being evolved. It gives true solns. in many solvents. The product from natural humic acid is very similar if not identical. With carbohydrate humic acid  $Cl$  gives a product,  $(C_{12}H_{11}O_{14}Cl)_x$ , pale yellow, amorphous powder, which differs from the product from hydroquinol humic acid in being insol. in  $Et_2O$ ,  $PhOH$ , etc., and in being stable towards  $H_2O$  and alkalis. Other solvents give colloidal solns.

C. J. WEST

Hemicelluloses. II. Ivory nut mannan. H. PRINGSHEIM and KARL SEIFERT. *Z. physiol. Chem.* 123, 205-12 (1922).—Mannan on hydrolysis gives mannose only. An acetate  $C_{12}H_{19}O_8$  was prepd. but mol. wt. detns. gave values from 2 to 4 times that called for by the formula.

R. L. STEHLE

Condensation of dehydrosesoxycholic acid. T. SHIMIZU. *Z. physiol. Chem.* 123, 159-63 (1922).—On passing  $HCl$  into a suspension of dehydrosesoxycholic acid in abs. alc. esterification and aldol condensation occur, and the  $OH$  group formed is replaced by  $Cl$ . The product,  $C_{22}H_{35}O_7Cl$  (I), m.  $204^\circ$  when crystd. from  $AcOH$ . Sapon and elimination of the  $Cl$  atom result from treatment with  $NaOEt$ . Acidification ppts. the free acid, which when crystd. from  $AcOEt$  m.  $276^\circ$ . Et dehydrosesoxycholate, m.  $108^\circ$ , may be obtained from the mother liquid of I by pptn. with  $H_2O$ . In prepg. the Me ester, m.  $130^\circ$ , no complications occur.

R. L. STEHLE

Deaminization of methyl *d*-cis-3-amino-1,2,2-trimethylcyclopentanoate. G. S. SKINNER. *J. Am. Chem. Soc.* 45, 1498-509 (1923); cf. *C. A.* 12, 478.—Decompn. with dil.  $HCl$  of diazotized Me *d*-cis-3-amino-1,2,2-trimethylcyclopentanoate (I) gives 62% unsatd. esters, 36%  $HO$  esters, 2%  $Cl$  esters, and no  $MeO$  acid; for the *trans*-isomer the corresponding values are 41, 46, —, 13%, resp. The products of decompn. of I, after extn. with  $NaHCO_3$  to remove any acid which might be present, were distd. under 3-8 mm. and sepd. into 10 fractions, each of which was sapond. with  $Na$  alcoholate and the free acids distd. *in vacuo* (except that from the highest boiling fraction, which was isolated as the  $Ca$  salt). The unsatd. acids are lauronic (II) and the 1,5,5-trimethyl- $\Delta^4$ -acid (III), which, based on the yields of the bromolactones, are present to the extent of approx. 70 and 30%, resp. Four cryst.  $HO$  acids were obtained: 65% of *d*-cis-2-hydroxy-1,2,3-trimethylcyclopentanoic acid (IV), 20% of *l*-trans-3-hydroxy-1,5,5-trimethylcyclopentanoic acid (V), 15% of *dl*-2-hydroxy-1,5,5-trimethylcyclopentanoic acid

(VI) and an acid (VII), m. 132–3°, obtained in too small amt. for identification. The HCl salt of the free acid of I is obtained in 85–90% yield from  $\alpha$ -*d*-camphoramidic acid with NaBrO<sub>3</sub>; 250 g. of this salt on esterification gives 115 g. of I.HCl, m. 237–8°,  $[\alpha]_D^{20}$  29.4° (0.05 g./cc. alc.), 29.2° (0.10 g./cc. alc.), 20.4° (0.04 g./cc. H<sub>2</sub>O). The yield of Et<sub>2</sub>O-sol. decompn. products is about 80%. The whole of the unsatd. esters boils within 5° and a fraction was obtained boiling within 0.5° (56° under 5.5 mm.) and yielding on sapon. a mixt. of acids (VIII), b<sub>4</sub> 108°, 5 g. of which with KMnO<sub>4</sub> gives 0.05 g. 1,2,2-trimethyl-1-carboxyglutaric acid. Again, 10 g. VIII with Br in CHCl<sub>3</sub> gives 5.5 g. of the di-Br deriv. (IX) of III, m. 189°,  $[\alpha]_D^{25}$  94.1°,  $[\alpha]_D^{29}$  91.6° (0.0994 g./cc. abs. alc.), which with Na<sub>2</sub>CO<sub>3</sub> gives a 2-bromolactone (X), m. 91–2° (cor.),  $[\alpha]_D^{25}$  –65° (0.04517 g./cc. abs. alc.). The residue from the CHCl<sub>3</sub> mother liquors from IX gives with Na<sub>2</sub>CO<sub>3</sub> a 1,2,3-trimethyl-2-bromolactone (XI), m. 194°,  $[\alpha]_D^{25}$  51°. X (1.5 g.) with NaOEt gives 0.7 g. of a HO lactone, m. 225–6°,  $[\alpha]_D^{25}$  0°. II prepd. from *d*-camphoric anhydride by Aschan's method b<sub>1</sub> 101–2°, showed  $[\alpha]_D^{19}$  197° and with Br in CHCl<sub>3</sub> gave only XI and no X, while a II prepd. by dry distn. of camphoric acid b<sub>1</sub> 108–10°, showed  $[\alpha]_D^{19}$  147°,  $[\alpha]_D^{23.5}$  117° (0.1 g./cc. abs. alc.) and yielded 11% of its wt. of X. With NaOEt, XI gives a 2,3-(HO)<sub>2</sub> acid, m. 174–5°, isolated in small amt. by pptn. from concd. Et<sub>2</sub>O soln. with petroleum ether and changing in contact with the mother liquors into the 2-HO lactone, m. 214–5°,  $[\alpha]_D^{25}$  0°. Me ester of IV, b<sub>1</sub> 88–9°, free IV, m. 102°,  $[\alpha]_D^{23}$  35.7° (0.0569 g./cc. abs. alc.). Me ester of VI, b<sub>1</sub> 108–10°, d<sub>4</sub><sup>20</sup> 1.0711,  $[\alpha]_D^{25.8}$  29.6° (0.967 g./cc. abs. alc.); free VI, m. 210°,  $[\alpha]_D^{25}$  0°, sublimes unchanged at 255°, behaves like *d*-cis-campholonic acid with Beckmann's CrO<sub>3</sub> mixt. but the resulting cryst. acid, m. 218°, gives no camphoric acid on further oxidation with KMnO<sub>4</sub>. Me ester of V, b<sub>1</sub> 105–7°,  $[\alpha]_D^{23}$  22.4°; free V, m. 121–2°, b<sub>1</sub> 165°,  $[\alpha]_D^{27}$  –10.3° (0.0329 g./cc. abs. alc.), is not converted into a lactone at 255°, gives with Beckmann's CrO<sub>3</sub> mixt. a liquid acid converted by further oxidation with KMnO<sub>4</sub> into camphoric acid, yields with HI in CS<sub>2</sub> an unstable iodide which with Na<sub>2</sub>CO<sub>3</sub> forms an unsatd. acid,  $[\alpha]_D^{35}$  35° (0.0091 g./cc. abs. alc.) and a small amt. of an inactive lactone, m. 47–8°. The probable course of the reactions involved in the deamination of I is discussed. C. A. R.

**Chemistry of polycyclic structures in relation to their homocyclic unsaturated isomeric.** IV. The simulation of benzenoid properties by the five-carbon intra-annular nucleus. CHRISTOPHER KELK INGOLD, ERNEST ARTHUR SEELEY and JOCELYN FIELD THORPE. *J. Chem. Soc.* 123, 853–74 (1923); cf. *C. A.* 16, 1217.—It is shown that it is possible so to adjust the stability of the phases in the 5-C series that the compds. do actually simulate in a marked degree the properties of aromatic compds. One means of reducing the stability of the bridged phase to the point at which the attack of various agents begins at the bridge was found to be the use of cyclohexane derivs. 5-Cyclohexanespirodiacyclo- $\Delta^2$ -pentan-3-one-1,2-dicarboxylic acid (I) (*C. A.* 13, 2016), upon oxidation with alk. K<sub>2</sub>Fe(CN)<sub>6</sub>, gives 5-cyclohexanespirocyclo- $\Delta^2$ -penten-3-ol-1,4-dione (II), C<sub>8</sub>H<sub>10</sub>:C.CO.CH:C(OH).CO, m. 134°, gives a cherry-red color with FeCl<sub>3</sub>, a

greenish blue Cu salt and titrates as a monobasic acid in the absence of carbonates. Anilino deriv., orange, m. 150–1°. Br deriv. (III), C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>Br, by rubbing II with Br and a little H<sub>2</sub>O, pale yellow, m. 190–1°; FeCl<sub>3</sub> gives a cherry-red color. With excess dry Br, either II or III gives a dibromotriketone, C<sub>8</sub>H<sub>10</sub>:C.CO.CBr<sub>2</sub>.CO.CO, yellow, de-

compd. above 100°; FeCl<sub>3</sub> gave no color reaction but cold dil. alkalis converted it into III. Oxidation of 5-cyclohexanespirodiacyclo- $\Delta^2$ -penten-3-ol-1-carboxylic acid (IV) gave II and  $\beta$ ,1-dicarboxy- $\beta$ ,1-cyclohexanecarboxylic anhydride (V); the free acid could not be fully purified; either product, heated with H<sub>2</sub>O in a sealed tube at 200°, gives cyclohexylidenesuccinic acid, m. 175°, and  $\alpha$ -hydroxy-1-carboxy- $\beta$ ,1-cyclohexanesuccinic acid lactone, m. 206°. I with alk. KMnO<sub>4</sub> gave (CO<sub>2</sub>H)<sub>2</sub> and  $\alpha$ -ketocyclohexane-1,1-diacetic acid (VI), m. 131°, the quinoxaline of which is orange-red, m. 146° (decompn.). The structure was established by reduction to  $\alpha$ -hydroxycyclohexane-1,1-diacetic acid. Oxidation of IV gave VI. The 4-Br deriv. of I results by treatment with 1.2 times the theoretical amt. of a 10% AcOH-Br soln., and m. 197–8°. Oxidation gave II and V. Hydrolysis with boiling alkali gave 1,3-dihydroxy-5-cyclohexanespirodiacyclo- $\Delta^2$ -pentene (VII), m. 179–80°, gives a marked red color with FeCl<sub>3</sub>, a blue Cu salt, liberates CO<sub>2</sub> from NaHCO<sub>3</sub>, does not react with NH<sub>4</sub>OH, PhNHNH<sub>2</sub>, etc., but gives brick-red azo dyes with PhN<sub>2</sub>X, etc. Oxidation with Br and NaOH gives 1-carboxycyclohexane-1-acetic acid, m. 132–3°. 2-Br deriv. (VIII), by the action of 2.2 atoms Br in CHCl<sub>3</sub>, m. 244° (decompn.); FeCl<sub>3</sub> gives an intense blood-red color. If I in AcOH is treated



with 1.5 times the theoretical amt. of Br and then satd. with HBr, the 2,4-di-Br deriv., m. 217-8°, results, FeCl<sub>3</sub> gives no color but gives an insol. Fe salt. Oxidation gave III. Hydrolysis gave a mixt. of VIII and of the corresponding 4-Br deriv. (IX), m. 228-9°; the 2 derivs. may be sepd. by their relative soly. in AcOEt. 4-Br deriv. of IV, m. 197-8°. Oxidation gave a mixt. of II and V. Hydrolysis yielded VII. 2,4-Di-Br deriv., m. 152-3°. Oxidation gave III and the Br deriv. of V, m. 155-8°. Hydrolysis gave IX. If IV is treated with Br and HBr, the 2,2,4-tri-Br deriv. results, m. 168-5°. Upon oxidation this gives III and upon hydrolysis VIII. Et ester of IV, b. 295°, m. 64.5-5°; semicarbazone, m. 183-5°. Oxidation with KMnO<sub>4</sub> gave VI, while K<sub>3</sub>Fe(CN)<sub>6</sub> gave II and V. Di-ethyl ester of I, b.<sub>20</sub> 236-8°; semicarbazone, m. 121-3°. Oxidation with KMnO<sub>4</sub> gave VI, with K<sub>3</sub>Fe(CN)<sub>6</sub> II and a small amt. of *cis*-cyclohexanespirocyclopropanedicarboxylic acid.

C. J. WEST

**Molecular models: benzene.** J. K. MORSE. *Phys. Rev.* 19, 243 (1922).—A 3-dimensional model of the C<sub>6</sub>H<sub>6</sub> mol. is constructed by arranging the C nuclei at the corners of a regular octahedron with edge  $x$ , the H atoms along the axes, 3 H nuclei located at a distance  $y$  and the other 3 nuclei at a distance  $z$  from their resp. corners. Three distinct axes:  $2x \cos 45^\circ + 2y$ ;  $2x \cos 45^\circ + 2z$  and  $2x \cos 45^\circ + y + z$  have lengths  $\sqrt{(na^2p)/(acN)}$ ,  $\sqrt{(na^2p)/(acNp)}$  and  $\sqrt{(na^2p)/(acN)}$  resp., where  $n$  = no. of mols. common to the elementary space lattice,  $\mu$  = mol. wt.,  $a$  and  $c$  = the crystallographic axial ratios,  $\rho$  = d., and  $N$  = Avogadro's no. From these data, and assuming  $x = 2.514 \times 10^{-8}$  (dtd. by Bragg), calcs. give  $y = 2.214 \times 10^{-8}$  and  $z = 3.212 \times 10^{-8}$  cm. By constructing models for C<sub>10</sub>H<sub>8</sub> and anthracene and substituting these values in the expression for their axes, axial ratios can be predicted which agree within exptl. limits with crystallographic measurements.

C. C. DAVIS

**Problem of substitution in the benzene nucleus and the Thomson-Lewis-Langmuir theory of covalence.** RONALD FRASER AND J. E. HUMPHREYS. *Chem. News* 126, 241-5, 257-61 (1923); cf. *C. A.* 17, 1957.—The earlier discussion is continued.

C. J. WEST

**Thermal treatment of aromatic hydrocarbons. II.** F. FISCHER, H. SCHRADER AND W. MEYER. *Ges. Abhandl. Kennnt. Kohle* 5, 413-51 (1920); cf. Fischer, *et al. Ges. Abhandl. Kennnt. Kohle* 4, 373 (1919).—The formation of BzOH from C<sub>6</sub>H<sub>6</sub> and CH<sub>4</sub>, C<sub>10</sub>H<sub>8</sub> from PhOH and CH<sub>4</sub>, PhOH from C<sub>6</sub>H<sub>6</sub> and water, and PhNH<sub>2</sub> from C<sub>6</sub>H<sub>6</sub> and NH<sub>3</sub> is demonstrated. The breaking down of a variety of complex mols. by the action of H is described, viz., PhNH<sub>2</sub>, Ph<sub>2</sub>, Ph<sub>2</sub>NH, CH<sub>2</sub>Ph<sub>2</sub>, fluorene, carbazole, phenanthrene, tetrahydronaphthalene, indene, acenaphthene, fluorene. The stability of C<sub>6</sub>H<sub>6</sub> homologs in a H atm. was studied; at high temps. a complete sepn. of the side chains occurred, the stability increasing in the order, cymene, xylene, PhMe, C<sub>6</sub>H<sub>5</sub>, C<sub>10</sub>H<sub>7</sub>Me was readily split up into CH<sub>4</sub> and C<sub>10</sub>H<sub>8</sub>. The action of H on a larger scale, and coal gas in contact with coke and C on lignite tar, anthracene oil, petroleum, low-temp. coal tar, and its hydrocarbon fraction (b. 230-300°), phenolic fraction (b. 200-50°), and cresotes, was examd.

J. S. C. I.

**Action of methyl sulfate on diphenylamine and on methyldiphenylamine.** C. S. GIBSON AND D. C. VINING. *J. Chem. Soc.* 123, 831-41 (1923).—In the prepn. of MeNPh<sub>2</sub> the best conditions are to heat a mixt. of 1 mol. Ph<sub>2</sub>NH and 1.5 mols. Me<sub>2</sub>SO<sub>4</sub> for about 10 min. on the H<sub>2</sub>O bath, and then run in aq. Na<sub>2</sub>CO<sub>3</sub> to the mechanically stirred liquid during 3 hrs. Unchanged Ph<sub>2</sub>NH is pptd. from the C<sub>6</sub>H<sub>6</sub> ext. by HCl and MeNPh<sub>2</sub> in 79.4% yield, then recovered by addn. of alkali; MeNPh<sub>2</sub>, b.<sub>10</sub> 145-5.5°, b.<sub>760</sub> 291-2°. In following Ullmann's directions it was found that there also resulted MeNPhC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, identical with that described by Cloez (*Compt. rend.* 124, 900 (1897)). The Na salt crystals with 2 H<sub>2</sub>O, the Mg salt with 6H<sub>2</sub>O; the Ag and Ba salts are anhydrous. Aniline salt, m. 179-80° and resolidifies at 195-6°, due to the formation of sulfanilic acid and MeNPh<sub>2</sub>. The best method for the prepn. of the Na salt is by the action of Me<sub>2</sub>SO<sub>4</sub> upon MeNPh<sub>2</sub> at 100° for 12 hrs. A 3rd product of the action of Me<sub>2</sub>SO<sub>4</sub> on Ph<sub>2</sub>NH is Me<sub>2</sub>NPh<sub>2</sub>OH (*Ber.* 36, 2487). Chloroplatinate, golden yellow, decomp. 180-2°. This base is obtained in 28% yield by heating 1 mol. each of MeNPh<sub>2</sub> and Me<sub>2</sub>SO<sub>4</sub> in 30 cc. C<sub>6</sub>H<sub>6</sub> at 100° for 12 hrs. and shaking with a satd. aq. soln. of 28 g. KI. EtNPh<sub>2</sub>, b.<sub>1</sub> 149.5-50°, was obtained in 35% yield from 1 mol. Ph<sub>2</sub>NH and 1.5 mols. Et<sub>2</sub>SO<sub>4</sub>; chloroplatinate, golden yellow, m. 166-9° (decompn.). No definite indications of the formation of a SO<sub>3</sub>H deriv. have been obtained.

C. J. WEST

**Action of phenylenediamine on  $\beta$ - and  $\gamma$ -trinitrotoluene.** MICHELE GRUA AND MARIO GRUA. *Gazz. chim. ital.* 53, 48-52 (1923).—The 3 isomeric C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub> react with the labile NO<sub>2</sub> group in  $\beta$ - and  $\gamma$ -C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub> (I and II) giving HNO<sub>2</sub> with which a 2nd mol. of C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub> reacts. In these expts. I and II were treated with 2 mols. of the base in EtOH. II + *o*-C<sub>6</sub>H<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub> at 50° gave 2,4-dinitro-5-methyl-2'-amino-

diphenylamine (III),  $C_{12}H_{11}O_2N_2$ , orange-yellow, m. 195–6°. III boiled a few mins. in EtOH with BzH gave the benzaldehydeimine,  $C_{12}H_{11}O_2N_2$ , orange-yellow, m. 214–5°. III heated with  $Ac_2O$  gave the *Ac deriv.*, yellow, m. 222–3°. III in cold AcOH treated with  $NaNO_2$  soln. gave 4',6-dinitro-*m*-tolylaziminobenzene (IV),  $N:N.C_6H_4.NC_6H_3-$

$Me(NO_2)_2$ , m. 164–5°. II with  $m-C_6H_4(NH_2)_2$  gave 2,4-dinitro-5-methyl-3'-amino-phenylamine, red-yellow, m. 160–1°; *Ac deriv.*, red-yellow, m. 224–5°. With  $p-C_6H_4(NH_2)_2$  II gave 2,4-dinitro-5-methyl-4'-aminodiphenylamine, garnet-red, m. 174–5°; *Ac deriv.*, red-yellow, m. 222–3°. With  $o-C_6H_4(NH_2)_2$  I gave 2,6-dinitro-5-methyl-2'-aminodiphenylamine (IV), garnet-red, m. 149–50°, of which the red benzaldehydeimine deriv.,  $C_{12}H_{11}O_2N_2$ , m. 173–4°. IV in AcOH with  $NaNO_2$  gave 2',6'-dinitro-*m*-tolylaziminobenzene, m. 166–7°. With  $p-C_6H_4(NH_2)_2$  I gave 2,6-dinitro-5-methyl-4'-aminodiphenylamine, garnet-red, m. 174–5°.

E. J. WITZEMANN

The action of benzalmethylamine on some aromatic nitro derivatives. MICHELÉ GIUA. *Gazz. chim. ital.* 53, 53–6 (1923).—In extending his studies of the behavior of  $NO_2$  compds. contg. a labile  $NO_2$ , G. studied the action of  $PhCH:NMe$  (I) on  $\beta$ - and  $\gamma$ - $C_6H_4(NO_2)_2$  (II) and (III), 3,4,6-( $O_2N$ ) $_3$  $C_6H_2Cl$  (IV) and ( $O_2N$ ) $_3$  $C_6H_2Br$  (V). The

first 2 compds. contain a labile  $NO_2$  that reacts with I thus:  $\text{>C}.NO_2 + 2I + H_2O \longrightarrow$

$\text{>C}.NHMe + 3BzH + CH_2O + N_2$ . In this reaction the  $HNO_3$  formed at first

reacts with the 2nd mol. of I, giving  $BzH + CH_2O + N_2$ . Thus I reacts like  $MeNH_2$  with compds. contg. labile  $NO_2$ . The Cl and Br derivs. react similarly. CIUSA (C. A. 5, 3804) observed that compds. contg. labile halogen atoms hydrolyze certain bases, like benzalazine, phenylhydrazones and  $PhN:CHPh$ . Tests with II and III on acetoxime,  $Ph_2C:NNHPh$  (VI) and  $PhN:CHPh$  showed no hydrolysis but VII formed addn. compds. that will be described later. 2.3 g. II in 30 cc. EtOH + 2.4 g. I boiled some mins. sepd. 4,6-dinitro-*m*-methyltoluidine (Brady, C. A. 15, 1280). The EtOH filtrate had the odor of BzH and gave crystals of BzOH. III similarly treated gave 2,4-dinitro-*m*-methyltoluidine (Brady *l. c.*). IV treated similarly sepd. 2,4-dinitro-5-chloromethyl-aniline (VII), orange-yellow, m. 106–7°. IV heated with excess of I in MeOH gave VII and some 4,6-dinitrodimethyl-*m*-phenylenediamine (VIII) (Blanksma, *et al.*, *Rec. trav. chim.* 21, 290 (1902)), yellow, m. 290° (decompn.), by replacement of the halogen atom also. V treated with I in EtOH gave 2,4-dinitro-5-bromomethyl-aniline, yellow, m. 149–50°. V treated with excess of I gave VIII also. E. J. WITZEMANN

Application of the Hofmann reaction to substituted carbamides. G. R. FELLIOTT. *J. Chem. Soc.* 123, 804–13 (1923).— $NaOH$  with  $PhNHCONHCl$  yields, as solid products,  $PhNHCONH_2$  and  $ClC_6H_4NHCONH_2$ ; the alk. filtrate, upon steam distn., gave  $p$ - $ClC_6H_4NHNH_2$  and  $C_6H_5Cl$ ; the residue of the distn., upon acidification, gave a yellow ppt. ( $p$ - $ClC_6H_4N:NCO_2H$  and  $p$ - $ClC_6H_4NHNHCO_2H$ ), which decompd. at once with vigorous gas evolution, leaving a yellow pasty mixt., contg.  $PhCl$ . The acid soln. contained  $p$ - $ClC_6H_4NHNH_2$ . Although these products were formed in very small quantity, there is little doubt that Hofmann's reaction had taken place. The filtrate from the action of  $NH_4OH$  upon  $PhNHCONHCl$  gave  $p$ - $ClC_6H_4N:NCONH_2$  and  $p$ - $ClC_6H_4NHNHCONH_2$ , m. 233°; the latter compd. is very susceptible to alk. oxidizing agents, yielding the former. EtOK and  $PhNHCONHCl$  gave  $p$ - $ClC_6H_4N:NCO_2K$ .  $NaOH$  and  $ClC_6H_4NHCONHCl$  at the b. p., gives 2,4,6- $C_6H_2Cl_3$ . The action in the cold, however, finally leads to 2,4,6-trichlorophenylhydrazine, m. 138°;  $HCl$  salt. The intermediate products are probably  $ClC_6H_4NHNHCO_2H$  and  $ClC_6H_4N:NCO_2H$ .  $NH_4OH$  gave only  $ClC_6H_4NHCONH_2$ . EtONa apparently gave  $ClC_6H_4NHNHCO_2Na$ , since it gave  $ClC_6H_4NHNH_2$  upon warming or treatment with  $HCl$ , and  $ClC_6H_4N:NCO_2Na$ . C. J. WEBB

Reactions of  $\alpha$ -phenyl- $\beta$ -hydroxyurea and of  $\alpha,\alpha$ -diphenyl- $\beta$ -hydroxyurea interpreted from the standpoint of their hydroxamic acid structure. C. DEW. HURD. *J. Am. Chem. Soc.* 45, 1472–89 (1923).—The prediction (C. A. 16, 415) that a compd. of the structure  $Ph_2NCONHOH$  (I) should form acyl derivs. whose salts should rearrange with great readiness in  $H_2O$  because "the relative ease of rearrangements of the Beckmann type is dependent upon the tendency for the radical, R, in the univalent N deriv.,  $RCON$ , to exist as a free radical" (in the present case R is  $Ph_2N$ ) has been amply verified. Derivs. of phenylcarbamylhydroxamic acid (" $\alpha$ -phenyl- $\beta$ -hydroxyurea") (II) could not be made to rearrange. The carbanilidophenylhydroxyurea structure,  $PhNHCONHOCONHPh$  (III), is given the preference over the diphenylhydroxybiuret struc-

ture,  $\text{PhNHCON(OH)CONHPh}$ , for the more stable compd. into which **II** easily changes. It is definitely proved that the assumption that **II**, in the formation of **III**, dissociates into  $\text{PhNCO}$  and  $\text{NH}_2\text{OH}$  is untenable.  $\text{NH}_2\text{CONHOH}$  and "hydroxybiuret" are similarly discussed in this connection. A preliminary study of the reaction between  $\text{PhNCO}$  and monohydroxamic acids seems to show that the addn. is at the  $\alpha$ - rather than at the  $\beta$ -hydroxylamino H. **II**, best prepd. by Kjellin's method, m.  $140^\circ$ , gives with alc.  $\text{Cu(OAc)}_2$  an abundant ppt. of a green Cu salt, the filtrate from which still gives a color reaction with  $\text{FeCl}_3$ . *Bz ester*, from 1.5 g. **II** partially dissolved in 0.5 g.  $\text{NaOH}$  in  $\text{H}_2\text{O}$  with  $\text{BzCl}$  or from **II** and an excess of  $\text{Bz}_2\text{O}$  at  $50^\circ$ , m.  $179^\circ$  (decompn.); if, in the 1st method of prepn., twice as much  $\text{NaOH}$  is used, the soln. of the **II** is not perceptibly hastened but its hydrolysis is increased; the filtrate from the *Bz ester* gives on neutralization a ppt. consisting chiefly of  $\text{BzNHOBz}$ , formed by the action of the  $\text{BzCl}$  on  $\text{NH}_2\text{OH}$ , which is obtained on hydrolyzing **II** with hot alkali. *K salt* of the *Bz ester*, from the ester with alc.  $\text{KOH}$ , blackens  $160$ – $80^\circ$  but does not change further below  $240^\circ$ ; boiled in  $\text{H}_2\text{O}$  it yields  $\text{CO(NHPh)}_2$ . *Ac ester*, from **II** and  $\text{Ac}_2\text{O}$  on the  $\text{H}_2\text{O}$  bath, m.  $121$ – $3^\circ$ , evolves gas  $135^\circ$ , insol. in dil.  $\text{NaOH}$ . *Acid Na salt*,  $[\text{PhNHCON(OAc)}]_2\text{HNa}$ , from the ester in alc. with  $\text{NaOMe}$ ; solns. in very dil.  $\text{NaOH}$  or in  $\text{H}_2\text{O}$  give on acidification **III** and on long standing crystals m.  $161^\circ$  (decompn.) which are neither  $\text{BzNHOBz}$  nor  $\text{CO(NHNHPh)}_2$  and yield **III** on soln. in concd.  $\text{H}_2\text{SO}_4$  and reprecip. with  $\text{H}_2\text{O}$ . *K salt*,  $\text{PhNHCONKOAc}$ . In prep. **III** by refluxing **II** in alc., no  $\text{PhNHCO}_2\text{Et}$  is formed, and in the presence of  $\text{PhNH}_2$  no  $\text{CO(NHPh)}$  is obtained. In  $\text{EtOAc}$ -petroleum ether,  $\text{BzNHOBz}$  and  $\text{PhNCO}$  do not react, but when the 2 compds. are heated together without a solvent they yield quant. the compd.  $\text{BzN(CONHPh)OCONHPh}$ , m.  $113$ – $4^\circ$ , converted into  $\text{CO(NHPh)}_2$  by heating alone over a free flame or in alc. with  $\text{NaOMe}$ . *Diphenylcarbamhydroxamic acid* (" $\alpha, \alpha$ -diphenyl- $\beta$ -hydroxyurea") (**I**), m.  $134$ – $4.5^\circ$ , is obtained in 15 g. yield from 23 g.  $\text{Ph}_2\text{NCOCl}$  and free  $\text{NH}_2\text{OH}$  in  $\text{C}_6\text{H}_6$  or in 9.5 g. yield from 13 g.  $\text{Ph}_2\text{NCOCl}$  and  $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4 + \text{NaOMe}$  in  $\text{MeOH}$ ; its colorless  $\text{H}_2\text{SO}_4$  soln. is colored intensely blue by a drop of  $\text{HNO}_3$ . *Ac ester*, obtained quant. like that of **II** above, m.  $126.5$ – $7.0^\circ$ , gives in  $\text{H}_2\text{SO}_4$  with  $\text{HNO}_3$  an intense blue color; *Na salt*, from the ester in abs. alc. with  $\text{NaOMe}$ , begins to decomp. in  $\text{H}_2\text{O}$  at room temp., with formation of  $\text{Ph}_2\text{NH}$  and  $\text{Ph}_2\text{NNH}_2$ ; the soln. from which it is originally pptd. yields on evapn. a little  $\text{CO(NHNHPh)}_2$ . *Bz ester*; *Na salt*.  $\text{PhNH(OH)}$  and  $\text{PhNCO}$  form  $\text{PhNHCON(OH)Ph}$  readily and in good yield and none of the isomeric **I**.

**Synthesis of diphenylguanidine.** J. D. BRUMBAUGH. *Chem. Age* (N. Y.) **31**, 175–6 (1923).— $\text{EtOH}$  (d. 0.87) at  $75^\circ$  is satd. with  $\text{NH}_3$ , and a mixt. of  $(\text{PhNH})_2\text{CS}$  and  $\text{ZnO}$  added, the temp. being maintained at  $75^\circ$  and  $\text{NH}_3$  passed through the stirred mixt. for 3 hrs., or until desulfurization is complete. The soln. is filtered hot and poured into dil.  $\text{NH}_4\text{OH}$ , which ppts. the  $(\text{PhNH})_2\text{C:NH}$ . The av. yield is 67%.

C. J. WEST

**Action of ferrous chloride on the hydrochlorides of some organic amines.** WM. M. CUMMING. *J. Soc. Chem. Ind.* **42**, 166–8T (1923).—In an attempt to sep. *o*- and *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$ , the action of  $\text{FeCl}_2$  was studied. No double salts were found but when a soln. of  $\text{FeCl}_2$  is added to satd. solns. of the  $\text{HCl}$  salts, several different cryst. modifications of the  $\text{HCl}$  salt are thrown out of soln. immediately or on scratching with a glass rod. The  $\text{HCl}$  salts without  $\text{FeCl}_2$  gave the same cryst. modifications depending upon the conditions of crystn. Up to 90% of the  $\text{HCl}$  salt in soln. was pptd. by the  $\text{FeCl}_2$ , the yield increasing with increase in vol. and concn. of the  $\text{FeCl}_2$  soln. Satd.  $\text{FeCl}_2$  had no action on satd. solns. of *o*-, *m*- and *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot 2\text{HCl}$ .  $\text{FeCl}_2$  ppts.  $(\text{C}_6\text{H}_4\text{NH}_2)_2 \cdot \text{HCl}$  from the di- $\text{HCl}$  salt; of the former 0.253 g. dissolves in 100 cc.  $\text{H}_2\text{O}$  at  $17^\circ$ , of the latter, 0.808 g. *o*-Tolidine  $\cdot 2\text{HCl}$ , which crystals from  $\text{H}_2\text{O}$  with  $1\text{H}_2\text{O}$ , crystals with 1.5  $\text{H}_2\text{O}$  in the presence of  $\text{FeCl}_2$ ; this hydrate is sol. to the extent of 5.76 g. in 100 cc.  $\text{H}_2\text{O}$  at  $17^\circ$ . In 5%  $\text{HCl}$ , 2.25 g.  $(\text{C}_6\text{H}_4\text{NH}_2)_2 \cdot 2\text{HCl}$  or 9.36 g.  $(\text{C}_6\text{H}_4\text{NH}_2)_2 \cdot \text{HCl}$  dissolve in 100 cc. at  $17^\circ$ .

C. J. WEST

**Phosphorus acid esters.** The influence of the character of the groups  $\text{R}'$ ,  $\text{R}''$ ,  $\text{R}'''$  on the stability of the molecular complexes  $\text{R}'\text{R}''\text{R}''' \cdot \text{COPCl}_2$  and  $\text{R}'\text{R}''\text{R}''' \cdot \text{COP(OH)}_2$ . I. D. R. BOYD AND GUY CHIGNELL. *J. Chem. Soc.* **123**, 813–7 (1923).—*Triphenylmethoxyphosphorus dichloride*,  $\text{Ph}_3\text{COPCl}_2$ , m.  $189$ – $90^\circ$  (decompn.), by adding  $\text{Ph}_3\text{COH}$  to  $\text{PCl}_5$  at  $0^\circ$  and after 0.5 hr. refluxing for 1 hr. Boiling  $\text{EtOH}$  for 0.5 hr. converts it into  $\text{Ph}_3\text{COEt}$ . Concd.  $\text{H}_2\text{SO}_4$  causes the evolution of  $\text{HCl}$ , and upon diln. with  $\text{H}_2\text{O}$ ,  $\text{Ph}_3\text{COH}$  is formed. With 8%  $\text{KOH-EtOH}$  at  $100^\circ$ , the free acid, decomp.  $237^\circ$ , is obtained. The Na salt is gelatinous. No decompn. occurs on boiling the aq. soln. even in the presence of excess of alkali.

C. J. WEST

**Arsenated derivatives of phenyldiketopyrrolidine.** J. R. JOHNSON WITH ROGER

ADAMS. *J. Am. Chem. Soc.* **45**, 1307-15 (1923).—The compd. (I) obtained by the action of  $\text{AcCO}_2\text{H}$  on  $p\text{-H}_2\text{NC}_6\text{H}_4\text{AsO}_2\text{H}_2$  (II) in hot alc. was described in an earlier paper as 2-phenylquinoline-4-carboxylic-6-arsonic acid (*C. A.* **16**, 422) because it loses approx. 1 mol.  $\text{CO}_2$  on heating at its decompn. temp., although by analogy with the reaction of  $p\text{-H}_2\text{NC}_6\text{H}_4\text{NO}_2$  with aldehydes and  $\text{AcCO}_2\text{H}$  and from the fact that on fusion with  $\text{NaOH}$  I gives  $\text{PhNH}_2$  as the chief nitrogenous product I might rather be expected to be 1-*p*-arsonophenyl-2-phenyl-4,5-diketopyrrolidine,  $\text{H}_2\text{O}_2\text{AsC}_6\text{H}_4\text{N}\cdot\text{CO}\cdot\text{COCH}_3\cdot\text{CHPh}$ , and

such it has now been proven to be, for the analogous 1-*p*- $\text{O}_2\text{NC}_6\text{H}_4$  compd. loses 0.63 mol.  $\text{CO}_2$  when boiled 15 min. with  $\text{BzOEt}$  and 0.95 mol. under the same conditions in the presence of an equal amt. of  $o\text{-O}_2\text{NC}_6\text{H}_4\text{AsO}_2\text{H}_2$ . The structure of I is further confirmed by the fact that I may be prepd. in  $\text{Et}_2\text{O}$  suspension as well as in alc. and with  $\text{AcCO}_2\text{Et}$  instead of the free  $\text{AcCO}_2\text{H}$ . Extension of the reaction with  $\text{AcCO}_2\text{H}$  to other aminoarylarsonic acids and other aldehydes has shown that the reaction is general for aromatic but not for the simple aliphatic aldehydes (paraldehyde,  $\text{PrCHO}$ ) and that it occurs with arsonic acids substituted in the *m*- and *p*-positions to the  $\text{NH}_2$  group but not with *o*-substituted acids, benzylideneamino derivs. being formed in the latter case. Preliminary pharmacological expts. with I show that it is much less toxic than arspenamine, but also that its trypanocidal action is much smaller. 2-Methoxyphenylarsonic acid (13.5 g. from 12.3 g.  $o\text{-MeOC}_6\text{H}_4\text{NH}_2$ ), m.  $193-4^\circ$ ; *p*-isomer, m.  $176-7^\circ$ . 2-Methoxy-4-nitrophenylarsonic acid, pale yellow, does not m.  $250^\circ$ , was prepd. from 2,4-MeO- $(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{NH}_2$ , m.  $136-9^\circ$ , which was obtained in 60% yield by nitration of  $o\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$ ; with  $\text{NH}_4\text{OH}\cdot\text{FeCl}_2$  it gives 60% of the 4- $\text{NH}_2$  acid (III), m. (decompn.)  $203-4^\circ$  on slow,  $208-9^\circ$  on rapid heating. The following 1-*p*-arsonophenyl-4,5-diketopyrrolidine derivs. were obtained in 50-70% yields (all m. with decompn.): 2-Ph (I), m.  $186-7^\circ$  (in its prepn. there is also obtained a small amt. of benzylidene-*p*-arsanilic acid, m.  $225^\circ$ ); 2-*o*-methoxyphenyl, from  $o\text{-MeOC}_6\text{H}_4\text{CHO}$ , II and  $\text{AcCO}_2\text{H}$ , pale yellow, m.  $173-6^\circ$ ; 2-*p*-methoxyphenyl, m.  $164-5^\circ$ ; 2-3',4'-methylenedioxyphenyl, light yellow, m.  $176-8^\circ$ ; 2-*p*-chlorophenyl, m.  $163-5^\circ$ . 1-[4'-Arsono-3'-methoxyphenyl]-2-phenyl-4,5-diketopyrrolidine, from 2,4-Me( $\text{H}_2\text{N}$ ) $\text{C}_6\text{H}_3\text{AsO}_2\text{H}_2$ ,  $\text{AcCO}_2\text{H}$  and  $\text{BzH}$ , cream-colored, m.  $180-6^\circ$  (decompn.); 1-[4'-arsono-3'-methoxyphenyl] compd., from III, yellow, m.  $175-6^\circ$  (decompn.). Benzylidene-*o*-arsanilic acid, from  $o\text{-H}_2\text{NC}_6\text{H}_4\text{AsO}_2\text{H}_2$ ,  $\text{BzH}$  and  $\text{AcCO}_2\text{H}$ , m.  $227-9^\circ$  (decompn.); 4-benzylamino-3-methoxyphenylarsonic acid, from 3,4-Me( $\text{H}_2\text{N}$ ) $\text{C}_6\text{H}_3\text{AsO}_2\text{H}_2$ , cream-colored, m.  $202-5^\circ$  (decompn.); 4-*p*-chlorobenzylamino-3-methoxyphenylarsonic acid, pale yellow, m.  $255-60^\circ$  (decompn.). C. A. R.

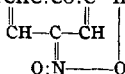
Preparation of the mercury compounds of the phenyl halides. M. E. HANKE. *J. Am. Chem. Soc.* **45**, 1321-30 (1923).—The halogenphenylmercuric acetates (I) can be obtained quickly, in good yields and in pure state by boiling the corresponding halogenbenzenesulfonic acid with 3 equivs.  $\text{Hg}(\text{OAc})_2$  in  $\text{AcOH}$ , filtering off the  $\text{Hg}^+$  salts formed and pptg. from the filtrate with  $\text{H}_2\text{O}$  or alkali; addn. of  $\text{NaCl}$  to their aq. or alc. solns. gives the corresponding chlorides. By refluxing Ph halides with 0.1 mol.  $\text{Hg}(\text{OAc})_2$  at  $140^\circ$  until the mixt. no longer gives a positive sulfide test for inorg.  $\text{Hg}$ , the *p*-I can easily be isolated in fairly good yield but the sepn. of the remaining *o*- and *m*- and possibly other compds. is extremely difficult and requires a tedious process of fractional crystn. In the *o*- and *p*-I, the  $\text{HgOAc}$  can readily be replaced by a  $\text{NO}_2$  group with 68%  $\text{HNO}_3$  at  $65^\circ$  but with the *m*-compds. the reaction is not so simple. The I prepd. by direct mercuration melt somewhat lower than those made from the  $\text{SO}_2\text{H}$  acids, possibly owing to the presence of persistent impurities which cannot well be removed by fractional crystn. The  $\text{SO}_2\text{H}$  acids were made from the corresponding anilines by the Gatterman method (diazotization and treatment with  $\text{SO}_2$  and catalytic  $\text{Cu}$ ). *p*-Chlorophenylmercuric acetate, m.  $193^\circ$ , is obtained in 70% yield from *p*- $\text{ClC}_6\text{H}_4\text{SO}_3\text{H}$ , m.  $99^\circ$ , and in about 40% yield by direct mercuration of  $\text{PhCl}$ ; chloride, m.  $225^\circ$ . *m*-Chlorophenylmercuric acetate, m.  $133^\circ$ , is similarly made from the sulfonic acid, m.  $81^\circ$ ; chloride, m.  $210^\circ$ . *o*-Chlorophenylmercuric acetate, m.  $115^\circ$ , is obtained in 70% yield from the sulfonic acid, m.  $120^\circ$ ; chloride, m.  $145^\circ$ . *p*-Bromophenylmercuric acetate, m.  $196^\circ$ , is obtained in 60% yield from the sulfonic acid, m.  $114^\circ$ , and in 25% yield directly from  $\text{PhBr}$ ; chloride, m.  $250^\circ$ . *m*-Bromophenylmercuric acetate, m.  $160^\circ$ , is obtained in 40% yield from the sulfonic acid, m.  $88^\circ$ ; chloride, m.  $198^\circ$ . *o*-Bromophenylmercuric acetate, m.  $124^\circ$ , is obtained in 68% yield from the sulfonic acid, m.  $130^\circ$ ; chloride, m.  $155^\circ$ . *p*-Iodophenylmercuric acetate, m.  $191^\circ$ , is obtained in 50% yield from the sulfonic acid, which seems to change state but does not m. completely at  $100^\circ$ , and in about 4% yield by direct mercuration of  $\text{PhI}$ . All the above acetates were identified by treating them in aq.  $\text{KBr}$  or  $\text{AcOH}$  with  $\text{Br}$ , whereby the  $\text{HgOAc}$  group is replaced by  $\text{Br}$  with formation of the corresponding dihalogenbenzene. In the direct mercur-

ation of PhBr, from the mother liquors from the *p*-BrC<sub>6</sub>H<sub>4</sub>HgOAc were also isolated the *o*- and *m*-isomers. C. A. R.

**Preparation of *p*-tolylmercury compounds.** F. C. WHITMORE, FRANCES H. HAMILTON AND NEAL THURMAN. *J. Am. Chem. Soc.* 45, 1066-8 (1923).—*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Na. 2H<sub>2</sub>O is obtained in 80-90% yield from Zn dust and MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl in hot H<sub>2</sub>O and subsequent treatment with Na<sub>2</sub>CO<sub>3</sub>; with HgCl<sub>2</sub> in boiling H<sub>2</sub>O it gives 60% MeC<sub>6</sub>H<sub>4</sub>HgCl, m. 230°, which, refluxed in alc. with a 75% excess of NaI, yields 80% (MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg, m. 235°. C. A. R.

**Reaction of organic mercury compounds with halides. I. Mercury di-*p*-tolyl and sulfonyl halides.** F. C. WHITMORE AND NEAL THURMAN. *J. Am. Chem. Soc.* 45, 1068-71 (1923).—*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>I, refluxed with (*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg (I) in CCl<sub>4</sub>, reacts partially to form (MeC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SO<sub>2</sub>, HgI<sub>2</sub> and MeC<sub>6</sub>H<sub>4</sub>HgI; the yield of sulfone, based on the material reacting, is almost quant. MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl does not react with I under the above conditions. At higher temps. in PhMe or xylene, MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl and PhSO<sub>2</sub>Cl react with I but give only traces of definite org. products. No PhHgCl is obtained from PhSO<sub>2</sub>Cl and I. C. A. R.

**Mercury derivatives of salicylaldehyde and the nitrosalicylaldehydes.** F. C. WHITMORE AND E. B. MIDDLETON. *J. Am. Chem. Soc.* 45, 1330-4 (1923).—Salicylaldehyde (I) with 2 mols. Hg(OAc)<sub>2</sub> in alc. AcOH on the H<sub>2</sub>O bath gives 3,5-diacetoxymercurisalicylaldehyde (II) (42 g. from 10 g. I), m. 234° (decompn.), sol. in about 5 parts boiling and 10 parts cold AcOH, sol. in aq. NaOH, loses all its Hg with boiling alc. KI, forming I and KOH, yields metallic Hg with NH<sub>4</sub>OH and PhNHNH<sub>2</sub>, gives in AcOH with chlorides the *dichloromercuri* compd., does not m. 270°. Even with 1 mol. Hg(OAc)<sub>2</sub> the main product is II, although a small amt. of the 3(?)-acetoxymercuri compd. is formed, isolated as the *chloromercuri* compd. (5 g. from 10 g. I), m. 189-90°, converted by I in CHCl<sub>3</sub> into 3(?),2-I(HO)C<sub>6</sub>H<sub>4</sub>CHO, m. 52-8°. 3-Acetoxymercuri-5-nitrosalicylaldehyde (III) (26 g. from 12 g. 5,2-O<sub>2</sub>N(HO)C<sub>6</sub>H<sub>4</sub>CHO), pale yellow, does not m. 260°, sol. in NaOH with yellow color. 5,3-Isomer (IV) (9 g. from 4 g. 3,2-O<sub>2</sub>N(HO)C<sub>6</sub>H<sub>4</sub>CHO), does not m. 260°. 3-Chloromercuri-5-nitro compd. (V) (8 g. from 10 g. III) does not m. 260°. The above mercurated I condense with primary aromatic amines to form colored Schiff bases. The 3,5-diacetoxymercurisalicylaldehydes of the following amines were prepd.: *aniline* (5.5 g. from 5 g. II), brick-red, amorphous, does not m. 260°; *p*-toluidine; *p*-aminobenzoic acid (yield, 5.5 g.), deep red, sol. in dil. alkali, AcOH reprecip. a substance richer in Hg (56.7%), possibly consisting of the anhydride or of a partially hydrolyzed product in which one of the AcOHg groups has been changed to HOHg; *anthranilic acid*. 3(?)-Chloromercurisalicylaldehyde (2 g. from 2 g. of the ClHg(HO)C<sub>6</sub>H<sub>4</sub>CHO), yellow, m. 182-4°. III in hot PhNH<sub>2</sub> gives on cooling a deep red amorphous compd. C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub>Hg, does not m. 250°, sol. in alkalis, which is probably an anhydride or inner salt, PhN:CHC.CO.C—Hg, formed between the acinitro and HOHg groups.



A similar product is formed from IV, while V condenses without anhydride formation, giving 3-chloromercuri-5-nitrosalicylaldehyde, orange-red. C. A. R.

**Preparation of potassium and sodium arylsulfoniodoamides.** ELWYN ROBERTS. *J. Chem. Soc.* 123, 849-53 (1923).—The sulfonamide in the min. amt. of 10% KOH (NaOH) is slowly added to an excess of I in aq. KI(NaI); 50% KOH (40% NaOH) is introduced drop by drop until the I and the periodide have disappeared. The salts immediately appear as a yellow cryst. powder. One may also add the alkali to an intimate mixt. of I and sulfonamide covered with a few cc. H<sub>2</sub>O. The yield varies between 50 and 85%. The salts decomp. slowly when exposed to the air; they have the characteristic hypoiodite odor. The H<sub>2</sub>O of crystn. is lost at 75° or over P<sub>2</sub>O<sub>5</sub>. When heated, the solid "explodes" at temps. varying with the salt and the rate of heating. H<sub>2</sub>O extensively hydrolyzes the salts, free I appearing and ultimately iodide, iodate and the sulfonamide are formed. The solns. show the reactions of a relatively stable hypoiodite. The following were prepd.: *K benzenesulfoniodoamide*, *K toluene-*p*-sulfoniodoamide*, *K and Na o-deriv.*, *K and Na naphthalene- $\alpha$ -sulfoniodoamide*, and the *K  $\beta$ -deriv.* Two periodides were prepd.: 3PhSO<sub>2</sub>NH<sub>2</sub>.KI.2I<sub>2</sub> and 3(*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub>).KI.3I<sub>2</sub>. C. J. WEST

**A synthesis of thymol from *p*-cymene. II.** MAX PHILLIPS. *J. Am. Chem. Soc.* 45, 1489-93 (1923); cf. C. A. 14, 2619.—The synthesis described in the earlier paper has been improved; the yields now obtained in the various steps indicate the possibility of utilizing *p*-cymene, the main constituent of so-called sulfite turpentine, as a source for

synthetic thymol. Nitrocymene with Fe powder-HCl in boiling  $H_2O$  gives 80-6% cymidine, which with fuming  $H_2SO_4$  at 130-40° yields 80% of the  $SO_3H$  acid; this on diazotization and treatment with  $SO_3$  gives 70-5% *cymylhydrazine-p-sulfonic acid*, m. 260° (decompn.) (Ba salt, light yellow plates with  $5H_2O$ );  $CuSO_4$  in boiling  $H_2O$  converts it into cymene-3-sulfonic acid, obtained in 79% yield as the Na salt, which, heated 0.5 hr. at 350° with 3 parts KOH, gives 59% thymol. C. A. R.

**The photosensitiveness of some urethans.** A. KORCZYNSKI WITH ST. GRZYBOWSKI. *Gazz. chim. ital.* 53, 94-9(1923).—In studying the influence of negative groups in the PhOH mol. on their action on  $Ph_2NCOCI$  to give urethans,  $ROCONPh$ , K. found that picric acid and 2,4-( $O_2N$ ) $_2C_6H_3OH$  give brown tars from which nothing could be isolated. With 4,2- $X(NO_2)C_6H_3OH$  a urethan was isolated that browns in the light. This photochem. reaction also takes place in neutral org. solvents in the presence or absence of  $O_2$ . A no. of urethans were synthesized in order to test their photosensitiveness. Only a few were found that show this property. Equimol. amts. of 4- $ClC_6H_4OH$  and  $Ph_2NCOCI$  were heated under a condenser for 3 hrs. On cooling the product was poured into dil.  $H_2SO_4$ . From the oil which seps. 4-chlorophenyl *N*-diphenylcarbamate, 4- $ClC_6H_4OCONPh$ , m. 97°, crystallizes in 24 hrs. The following esters were obtained similarly: 4-bromophenyl, m. 99°; 4-iodophenyl, m. 126-7°; 2,4,6-trichlorophenyl, m. 143°; 2-nitrophenyl, m. 108-9°; 4-nitrophenyl, m. 112°; 4-nitro-2,6-dichlorophenyl, m. 132°; 2-nitro-4-chlorophenyl (I), m. 124-5°; 2-nitro-6-bromo-4-chlorophenyl (II), m. 140°; 2-nitro-4,6-dibromophenyl (III), m. 139°; 2-nitro-4,6-diodophenyl, m. 174-5°; 2-nitro-4-bromophenyl (IV), m. 129-30°. Of the above I, II, III and IV are photosensitive, IV, being the most sensitive. Details about the transformation of IV in the solid state and in soln. are given. The changes with these urethans are more profound than the photochem. change of  $o-O_2NC_6H_4CHO$  into  $o-ONC_6H_4CO_2H$  or  $PhCH:N(:O)Ph$  into  $PhCONHPh$  (Alessandri, *C. A.* 5, 276). K. and G. think that probably an azoxy compd. and other products of more complicated decompn. are formed. The product was sapond. with alc. KOH and distd. with steam giving  $Ph_2NH$ , which proves that the PhN radical in these urethans is not attached in the photochem. transformation. E. J. WITZEMANN

**Oxidation of benzeneazoresorcinol.** DINO BIGIARI AND GIULIO GIANNINI. *Atti accad. Lincei* [v] 31, ii, 109-16(1922).—Of the 2 di-Ac derivs., (a)  $PhNO:NCH_2(OAc)_2$ , and (b)  $PhN:NOC_6H_4(OAc)_2$ , obtainable by the oxidation of the diacetate of benzeneazoresorcinol by means of  $H_2O_2$ , only the latter is actually obtained, the  $\alpha$ -form probably undergoing further oxidation.  $\beta$ -4-Benzeneazoxyresorcinol, 2,4-(HO) $_2C_6H_3NO:NPh$ , red, m. 144°, giving a chestnut-yellow powder. The dibenzoate, pale yellow, m. 113°, diacetate, pale yellow, m. 102°. 4-Benzeneazoxy-2,6-dibromoresorcinol,  $PhN:NOC_6H_2Br_2(OH)_2$ , greenish yellow, m. 153°, and yields  $PhNH_2$  when reduced with Zn and AcOH. 4- $\alpha$ , $\beta$ -Dibromobenzeneazoxy-2,6-dibromoresorcinol,  $C_6H_2O_2N_2Br_4$ , red, m. 229° (decompn.), and gives 2,4- $Br_2C_6H_3NH_2$  when reduced with Sn and HCl. 2,6-Dibenzeneazoxy-4-benzeneazoxyresorcinol,  $PhN_2OC_6H(OH)_2(N_2Ph)_2$ , red, m. 220°. With alc. KOH, the diacetate of  $\beta$ -benzeneazoxyresorcinol yields a dark red compd., m. about 190°, which has not yet been characterized. J. C. S.

**Electrolytic oxidation of benzene to quinone and the electrolytic reduction of quinone.** A. SEYEWERTZ AND G. MIONDON. *Bull. soc. chim.* 33, 449-58(1923).—S. and M. obtained a yield of 65%  $C_6H_4O_2$  by employing Pb electrodes, sepd. by a porous earthenware diaphragm, and an electrolyte consisting of 25%  $H_2SO_4$  (66° Bé.) and 33% AcOH, in which was emulsified by continuous stirring  $\frac{2}{3}$  of its vol. of  $C_6H_6$ . Finely divided  $PbSO_4$  (1-1.5%) was employed as catalyst, and the concn. of  $C_6H_4O_2$  was not allowed to exceed 1%. The cell was operated at 24° with a c. d. of 4 amps./dm.<sup>2</sup> and a voltage of 3.2-3.5 v.  $C_6H_4O_2$  may be reduced quant. to hydroquinol in a similar electrolyte at 40°, 1% vanadic acid being added as catalyst, or the  $C_6H_4O_2$  soln. of  $C_6H_4O_2$  as formed allowed to flow from the anode to the cathode compartment, there being reduced to  $C_6H_4O_2$ . A. C. PURDY

**Platinum oxide as a catalyst in the reduction of organic compounds. II. Reduction of aldehydes. Activation of the catalyst by the salts of certain metals.** W. H. CAROTHERS WITH ROGER ADAMS. *J. Am. Chem. Soc.* 45, 1071-86(1923); cf. *C. A.* 16, 2500.—Pt black from  $PtO_3$  prepd. from absolutely pure  $H_2PtCl_6$  very quickly becomes inactive when shaken with an aldehyde in a H atm.; only by frequent reactivation can the reduction be carried to completion. The addn. of as little as 4 parts per million of Fe as  $FeCl_2$  or  $FeCl_3$  greatly accelerates the reduction. A systematic study of the effect of various amts. of  $FeCl_2$  and  $FeCl_3$  on the catalytic reduction of BzH and of  $FeCl_3$  on that of heptaldehyde, using the  $PtO_3$  catalyst described in the 1st paper, has shown that the optimum effect is obtained when the amt. of Fe chloride present is

approx. 0.0001 mol. in 100 cc. of the reaction mixt. With higher concns. of  $\text{FeCl}_3$  the only additional effect is a very slight diminution in the rate of reduction and a tendency for the reduction to proceed beyond the alc. stage.  $\text{FeCl}_3$  is first reduced to  $\text{FeCl}_2$ . With not more than 0.0001 mol.  $\text{FeCl}_3$  the effect is quite similar to that produced by  $\text{FeCl}_2$ ; with larger amts. an induction period appears and the reduction becomes slower because of the  $\text{HCl}$  set free in the reduction of the  $\text{FeCl}_3$ . The reduction proceeds beyond the formation of  $\text{PhCH}_2\text{OH}$  to  $\text{PhMe}$  and even further. Foreign materials sufficient to increase the activity of the catalyst appreciably accumulate during its recovery, even when C. P. reagents are used and every precaution is taken to guard against the introduction of accidental impurity. There is evidence that the inactivity of pure Pt black is due to its being deprived of the O necessary for its activity by the readily oxidizable aldehyde; the Fe salt specifically inhibits this reaction and thus prolongs the active life of the catalyst. With appropriate amts. of  $\text{FeCl}_3$  and 0.23 g. catalyst, 21.2 g.  $\text{BzH}$  can be smoothly reduced to the alc. in 20-5 min.; the reaction then stops and no further reduction takes place. A method is described for reducing 100 g.  $\text{BzH}$  in 4 hrs. with 0.025 g. catalyst.

C. A. R.

**Derivatives of 2,4-dinitrobenzaldehyde.** III. T. B. DOWNNEY WITH ALEXANDER LOWY. *J. Am. Chem. Soc.* 45, 1060-5 (1923); cf. C. A. 15, 1527.—The 2,4-dinitrobenzal derivs. of the following amines were obtained in about 90% yield from 1 mol. each of the aldehyde and the amine in alc. on the  $\text{H}_2\text{O}$  bath: 2,4-dichloroaniline, bright orange, m. 185°; o-chloroaniline, yellow, m. 167.5°; p-isomer, yellow, m. 161.5°; p-aminoazobenzene, red, m. 229°; o-tolidine (I) (prepd. in  $\text{AcOH}$ ), yellowish red, m. 289° (decompn.). In the last case, when the condensation was effected in alc. there was obtained the intermediate deep purple addn. product,  $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{CHO} \cdot \text{H}_2\text{NC}_6\text{H}_4\text{Me} \cdot \text{C}_6\text{H}_4\text{MeNH}_2$ , m. 232°, which with a little  $\text{AcOH}$  in  $\text{Me}_2\text{CO}$  gives I and with hot  $\text{Ac}_2\text{O}$  yields the orange-yellow *Ac* deriv. of I, m. 231.5°. Refluxed in  $\text{AcOH-HCl}$  with 2 mols. of a phenol or condensed with 2 mols. of a tert. arom. amine with  $\text{ZnCl}_2$  or concd.  $\text{HCl}$  the aldehyde gave the following 4,4'-(2,2'-dinitrophenylmethylene) derivs.: bisphenol (II),  $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{CH}(\text{C}_6\text{H}_4\text{OH})_2$ , yellow, m. 204°, oxidizes in the air to an orange product, forms a brick-red Na salt, acts as an indicator towards acids (pale yellow) and the normal carbonates and the hydroxides of the alkali metals (red) (yield, 10 g. from 6 g.  $\text{PhOH}$ ); bis-o-chlorophenol, yellow, m. 190.5° (yield, 80%); bis-o-cresol, yellow, m. 200.5° (yield 75%); bisguaiacol, yellow, m. 221° (yield, 65%); bisallylic acid, yellow, m. 268.5°, (yield, 40%); bisresorcinol (III), yellow, becomes red 210-5°, gradually chars above 280° (yield, 4 g. from 7 g.  $m\text{-C}_6\text{H}_4(\text{OH})_2$ ), forms a dark red Ca salt,  $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{CH}(\text{C}_6\text{H}_3\text{O}_2\text{Ca})_2$ ; bisdimethylaniline (2,4-dinitro-malachite green), yellow, m. 151.5° (yield, 80%), oxidized to the color base and dye by the usual methods, both the  $\text{ZnCl}_2$  salt and the oxalate dyeing silk and wool a blue-green without mordanting; bisdiethylamine (2,4-dinitro-brilliant green), dirty green; bisbenzylethylaniline, brownish yellow (yield, 32%). Tetrabromo deriv. of II, from II and Br in  $\text{AcOH}$ , yellow, m. 234°; yield, 70%. The mother liquors from III yield the yellowish red amorphous o-[2,4-dinitrophenyl]-3,6-dihydroxyxanthene, also obtained from the aldehyde and  $m\text{-C}_6\text{H}_4(\text{OH})_2$  with  $\text{ZnCl}_2$  at 95-130° or with concd.  $\text{H}_2\text{SO}_4$  at 60°, forms deep red Na, K and  $\text{NH}_4$  salts; Ca salt; tetrabromo deriv., red, chars above 290°, forms Na and K salts sol. in  $\text{H}_2\text{O}$  with deep red color.

C. A. R.

**The reaction of nitrosyl chloride on toluene.** E. V. LYNN AND HELEN L. ARKLEY. *J. Am. Chem. Soc.* 45, 1045-7 (1923); cf. C. A. 16, 1562.— $\text{PhMe}$  satd. with  $\text{NOCl}$  (about 3% by wt. of the  $\text{PhMe}$ ) readily reacts in sunlight below 10° according to the equation  $\text{PhMe} + \text{NOCl} \rightarrow \text{PhCH}_2\text{NO} + \text{HCl} \rightarrow \text{PhCH:NOH} \cdot \text{HCl}$ ; the crystals of the latter compd. are obtained in practically quant. yield.

C. A. R.

**Mechanism of chemical reactions. I. Reduction of amides and oxidation of amines.** KARL KINDLER. *Ann.* 431, 187-230 (1923).—In the formation of  $\text{RC}(\text{S})\text{NH}_2$  from  $\text{RCN}$  and  $\text{H}_2\text{S}$ , the assumption that  $\text{RC}(\text{NH})\text{NH}_2$  is an intermediate product is supported by the fact that in place of  $\text{NH}_4\text{HS}$ ,  $\text{Me}_2\text{NH}_2\text{HS}$  may be used in the synthesis of  $\text{PhCSNH}_2$ . The relative efficiencies of various catalysts in the reaction  $\text{H}_2\text{S}$  and  $\text{PhCH}_2\text{CN}$  are:  $\text{NH}_4\text{HS}$ , 77;  $\text{Me}_2\text{NH}_2\text{HS}$ , 81;  $\text{NaHS}$ , 89;  $\text{KHS}$ , 91. In general the prepn. of thioamides is favored by the catalytic effect of  $\text{NaHS}$  or  $\text{KHS}$  in  $\text{EtOH}$  or  $\text{Me}_2\text{NH}_2\text{S}$  in  $\text{C}_6\text{H}_6$  and by the exclusion of  $\text{H}_2\text{O}$  and a high concn. of  $\text{H}_2\text{S}$ . Tables of yields are given. Phenylthiopropionamide, m. 87°.  $\text{MeCSNH}_2$ , m. 115° (not 107-8°). Phenylselenoacetamide, m. 92-2.5°, from  $\text{H}_2\text{Se}$  and  $\text{PhCH}_2\text{CN}$ . Selenoacetamide, m. 126-6.5°, (17% yield).  $\text{P}_2\text{S}_5$  forms addn. compds. with certain amides (the *N*-dimethylbenzamide and *N*-dimethylphenylacetamide complexes form as thick oils), which are decompd. by  $\text{H}_2\text{O}$  into the original amide,  $\text{P}_2\text{O}_5$  and  $\text{H}_2\text{S}$  or upon heating into the corresponding thioamide. Addn. of  $\text{K}_2\text{S}$  increases the yield of the thioamide, examples of

which are given. *N*-Methylphenylthioacetamide, m. 62.5–3° (cor.). *N*-Dimethylthioacetamide,  $b_{11}$  180–2°, m. 67°. *N*-Dimethylphenylphenylthioacetamide, m. 80–1°. *N*-Dimethylphenylthioacetamide, reddish oil. The reduction of  $\text{PhCH}_2\text{CONH}_2$  by Na and  $\text{AlOH}$  gives in addn. to  $\text{PhCH}_2\text{CH}_2\text{NH}_2$  a small amt. of  $(\text{PhCH}_2\text{CH}_2)_2\text{NH}$ . The reduction of primary thioamides by Al-Hg proceeds with good yields in either EtOH or Et<sub>2</sub>O if the reducing agent is added in small portions. Di- $[\gamma$ -phenylpropyl]amine  $b_{12}$  245°; HCl salt, m. 203°. The electrolytic reduction of  $\text{PhCH}_2\text{CSNH}_2$  in EtOH-HCl, with 6.5 amp. and 8 volts for 4 hrs., gives 63% of  $\text{PhCH}_2\text{CH}_2\text{NH}_2$ .  $\text{PhCSNH}_2$  (2 g.) in 50% AcOH with Fe powder (4 days at 50–60°) gives 1 g. BzH (1.05 g.  $\text{PhCSNH}_2$  were recovered). Reduction in the presence of EtNH<sub>2</sub> or Me<sub>2</sub>NH leads to a reaction of the base with the intermediate product, and the formation of *N*-Et or *N*-Me<sub>2</sub> derivs. Thus  $\text{PhCH}_2\text{CSNH}_2$  gives a mixt. of  $\text{PhCH}_2\text{CH}_2\text{NH}_2$ ,  $(\text{PhCH}_2\text{CH}_2)_2\text{NH}$  and  $\text{EtPhCH}_2\text{CH}_2\text{NH}$ . *N*-Ethyl- $\beta$ -phenylethylamine hydrochloride, m. 182°. The reaction of *N*-dialkylthioamides at 30–40°, using 60% H<sub>2</sub>SO<sub>4</sub>, Pb electrodes, and a current of 0.3 amp. and 16 volts for 3–4 hrs., gives *tert.* amines in 75–100% yield. *N*-Monoalkylthioamides are reduced under the same conditions to sec. amines. With 80% H<sub>2</sub>SO<sub>4</sub> and a current of 0.15 amp., aldimines and aldehydes are obtained.  $\text{PhCONH}_2$  may be identified as one of the oxidation products of  $\text{PhCH}_2\text{NH}_2$ . This reaction is more readily carried out with the thioamides.  $\text{PhCH}_2\text{NMe}_2$ , heated in a sealed tube with S for 4 hrs. at 180°, gives  $\text{PhCSNMe}_2$ . Thioamides also result by the action of S upon the reaction products of aldehydes and ketones with NH<sub>3</sub> and amines. BzH, NH<sub>3</sub>, and S give  $\text{PhCSNH}_2$ . *p*-MeC<sub>6</sub>H<sub>4</sub>CHO and MeNH<sub>2</sub> with S give *N*-methylthio-*p*-toluamide, m. 55°. *N*- $\beta$ -Naphthylthiobenzamide, m. 106–7°. *N*-Dimethylthiobenzamide,  $b_{11}$  194°. *N*-Dimethylthio-*p*-methoxybenzamide, m. 68.5°. *N*-Dimethylthio-*p*-methoxyphenylacetamide, m. 75–6°. *N*-Dimethylthiophenylacetamide,  $b_{12}$  184°. *N*-Diethylthio-*p*-methoxyphenylacetamide,  $b_{12}$  220°. *p*-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>,  $b_{11}$  129–30°, gives *N*-methylthio-*p*-methoxybenzamide, m. 108–9°.  $\text{PhMeC:NMe}_2$ ,  $b_{10}$  96°. *p*-Nitro-*N*-dimethylphenylthioacetamide, m. 131° (90% yield). Reduction gives [*p*-aminophenyl]ethyl]dimethylamine,  $b_1$  137–8°, m. 40–2°; HCl salt, m. 261°. This gives 95% bordenine on diazotizing and heating. *N*-Methylhomopiperonylthioamide, m. 106°. The thioamide, m. 136°. Electrolytic reduction gives *N*-methylhomopiperonylamine, which may be transformed into hydrastinine (C. A. 7, 1511). Discussion of the formation of amines and amides in plant cells follows the theoretical discussion.

C. J. WEST

**Organic compounds containing sulfur. I. The effect on general absorption due to the valency and mode of linkage of the sulfur atom.** D. T. GIBSON, HUGH GRAHAM AND JAMES REID. *J. Chem. Soc.* 123, 874–81(1923).—A substance contg. in the mol. unsatd. S in "straight chain conjugation" with C<sub>6</sub>H<sub>5</sub> centers of unsatn. shows greater general absorption than a similar substance into the mol. of which "crossed conjugation" has been introduced. Certain compds. in which S is present in the mol. as a member of a ring system show anomalous general absorption compared with open-chain compds. The residual affinity of a S atom in a mol. is accountable, in part, for the alterations of those vibrations of the C<sub>6</sub>H<sub>5</sub> nucleus which give rise to selective absorption. Absorption spectra are given for Ph<sub>2</sub>S<sub>2</sub>, Ph<sub>2</sub>S<sub>2</sub>O<sub>2</sub>, Ph<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, Ph<sub>2</sub>S, Ph<sub>2</sub>SO, Ph<sub>2</sub>SO<sub>2</sub>, (PhCH<sub>2</sub>)<sub>2</sub>S, (PhCH<sub>2</sub>)<sub>2</sub>SO, (PhCH<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>, thianthrene, thianthrene sulfoxide, 1,4-thioxan, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S<sub>2</sub>O<sub>2</sub>, PhSO<sub>2</sub>H, PhSO<sub>2</sub>Na and PhMeSO<sub>2</sub>.

C. J. WEST

**Catalytic reduction of nitro compounds. I.  $\alpha,\beta$ -Unsaturated nitro compounds.** E. P. KOHLER AND N. L. DRAKE. *J. Am. Chem. Soc.* 45, 1281–9(1923).—Reduction of  $\text{PhCH:CHNO}_2$  in pure alc. or Et<sub>2</sub>O with H and Loew's Pt black gave chiefly Sonn and Schellenberg's dimol. product [ $\text{CHPh}(\text{CH}_2\text{NO}_2)_2$ ], m. 235–49° (C. A. 12, 1290) but in the presence of mineral acids the formation of this compd. is largely prevented and there are obtained 2 isomeric  $\text{PhCH}_2\text{CH:NOH}$ , m. 97° and 100°. Kelber's Ni catalyst (C. A. 11, 2798) gives practically the same results as Pt black.  $\text{PhCH:C(NO}_2)_2$ Ph with Pt black in Et<sub>2</sub>O gives only  $\text{PhCH}_2\text{CPh:NOH}$  (almost quant.) and no dimol. product.  $\text{Ph}_3\text{C:CHNO}_2$  with Willstätter's Pt black in dry Et<sub>2</sub>O quant. yields cryst. diphenylacetaldimine,  $\text{Ph}_3\text{CHCH:NH}$ , which is oxidized by CrO<sub>2</sub>-AcOH to  $\text{Ph}_3\text{CO}$ , forms with NH<sub>2</sub>OH and H<sub>2</sub>NCONHNH<sub>2</sub> the oxime and semicarbazone of  $\text{Ph}_3\text{CHCHO}$ , and at 90° loses NH<sub>3</sub> with formation of a compd., probably  $(\text{Ph}_3\text{CHCH:N})_2\text{CCHCHPh}$ , m. about 129° (decompu.).  $\text{Ph}_3\text{C:C(NO}_2)_2$  poisoned the catalyst so badly that it was not possible to complete the reduction; the products isolated in partial reductions were  $(\text{CPh}_2\text{CN})_2$  and  $\text{Ph}_3\text{CHCN}$ . Wieland from  $\text{PhC(NO}_2)_2\text{:C(NO}_2)_2\text{Ph}$  obtained tetraphenylpiperazine, NH<sub>2</sub>, and a little  $\text{PhCH}_2\text{CPh:NOH}$  (C. A. 15, 2857). These results indicate that  $\alpha,\beta$ -unsatd. NO<sub>2</sub> compds. behave towards reducing agents exactly like  $\alpha,\beta$ -unsatd. ketones. The primary reduction product is always a satd. NO<sub>2</sub> compd. In exceptional cases this is a dimol. compd. but as a rule it is the monomol. compd. formed by addn.



of 2 atoms of H either to the ethylene linkage or, more probably, to the conjugated system. The  $\text{NO}_2$  group, however, is reduced much more easily than the CO group and the primary products can therefore be isolated much more rarely in the case of the  $\text{NO}_2$  compds. than in that of the ketones. The  $\text{NO}_2$  group, moreover, is reducible in steps, and the intermediate products between the  $\text{NO}_2$  compds. and the amines vary as much in stability and soly. as in relative ease of reduction. The final result, therefore, depends in part on the structure of the  $\text{NO}_2$  compd., which det. the stability and mode of rearrangement of the intermediate products, and in part on external factors (soly., nature of the solvent, activity of the catalyst), which affect the extent of the reduction.  $\text{PhCH}(\text{CH}(\text{NO}_2))\text{CHBr}$  gave as one of the products of its reduction in

MeOH with Pt black  $\text{PhCH}(\text{CH}_2\text{NO}_2)\text{CH}_2\text{Br}$ , m. 98-9°, and thus behaves like the above nitroethylene derivs.

C. A. R.

The two forms of *o*-methylcyclohexanol. I. MASCARELLI. *Atti accad. Lincei* [v], 31, ii, 116-18(1922).—Since the mol. of *o*-methylcyclohexanol contains 2 asym. C atoms having unequal rotatory values, 4 optically active and 2 racemic forms of this compd. should exist. The compds. obtained by Godchot and Bédos (C. A. 16, 1942) and by Sabatier and Mailhe (*Compt. rend.* 140, 350-2(1905)) probably represent the 2 racemides. The cycloheptylcycloheptanol prep'd. by Godchot and Brun (C. A. 16, 2123) should exhibit similar optical isomerism to *o*-methylcyclohexanol. An analogous case is presented by the 2 modifications of decahydro- $\beta$ -naphthol (cf. Mascarelli, C. A. 6, 83; Mascarelli and Recusani, C. A. 6, 3096).

J. C. S.

The oxidation of 1,3,4-dimethylcyclohexanone and the synthesis of cyclopentane diketones. MARCET, GODCHOT. *Compt. rend.* 176, 1151-3(1923).—Oxidation of a 3% soln. of 1,3,4-dimethylcyclohexanone with  $\text{KMnO}_4$  gave a 90% yield of  $\gamma$ -methyl- $\delta$ -acetylvaleric acid,  $b_{10}$  177°,  $d_{17}$  1.078,  $n_D^{20}$  1.4599; semicarbazone, m. 136°; ethyl ester (I),  $b_{11}$  130,  $d_{17}$  0.9715,  $n_D^{20}$  1.4334. At the same time a small amt. of  $\beta$ -methyladipic acid was formed. The action of  $\text{H}_2\text{SO}_4$  on I gave  $\alpha$ -acetyl- $\beta$ -methylcyclopentane (II),  $\text{CO} \cdot \text{CHAc} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2$ ,  $b_{11}$  89-90°,  $d_{16}$  1.029,  $n_D^{16}$  1.4756, giving with  $\text{FeCl}_3$  a

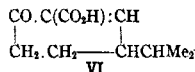
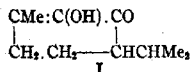
deep violet color. Semicarbazide with II gives 2 compds., one slightly sol. in alc., m. 240° (decompn.), and the other very sol. in alc., m. 120°. The H attached to the C between the 2 CO groups of I can be substituted by Na, and the resulting salt reacts with  $\text{EtI}$  to give  $\alpha$ , $\beta$ -dimethyl- $\alpha$ -acetylcyclopentanone (III),  $b_{14}$  99-100°,  $d_{17}$  1.020,  $n_D^{17}$  1.4585; semicarbazone, m. 240° (decompn.). The action of aq. KOH upon III gives  $\gamma$ -methyl- $\delta$ -acetylcaproic acid,  $b_{10}$  164° (decompn.),  $[\alpha]_{16}$  1.055,  $n_D^{16}$  1.4631; *Et ester*,  $b_{11}$  134-5°,  $d_{15}$  0.9865,  $n_D^{15}$  1.4488.

T. S. CARSWELL

Bird-lime. III. YUSHICHI NISHIZAWA. *J. Chem. Soc. Japan* 43, 810-7(1922); cf. C. A. 16, 1936.—In order to study the nature of mochiol, the unsaponifiable matter of bird-lime, dehydration of the substance was attempted. Since preliminary expts. showed that the product obtained from pure mochiol has similar phys. and chem. properties to those obtained from bird-lime, the original bird-lime was used without first isolating mochiol from it. "White" bird-lime mixed with lime (2:1) was heated in a retort. After distn. of  $\text{H}_2\text{O}$ , a pale greenish oil with a terpene odor distd. over at 120°. At 280-300°, the distillate had a red brownish color and easily solidified on cooling. The distillates at lower temps. are colorless transparent oils, the portion b. 112° has a beautiful bluish color becoming brown on exposure to air; the most of the oil, b. 132-52°, and the portion  $b_{60}$  160-80° has  $d_{25.15}$  0.8635. This oil was redistd.; the portions  $b_{48}$  155-60° and 165-70° have the compn.  $\text{C}_{14}\text{H}_{22}\text{O}$  or  $\text{C}_{14}\text{H}_{20}\text{O}$ . Neither gives an aldehyde reaction. This unsatd. compd., in 2-3 vols. cold  $\text{CHCl}_3$ , was satd. with  $\text{O}_2$ . During ozonization, the yellow or light blue soln. becomes brownish and opaque, and again becomes transparent on further ozonization (80 cc. oil absorbs 8.3 g. of  $\text{O}_3$ ). The ozonide can be decompd. by  $\text{H}_2\text{O}$  and heat. The resulting aldehyde gives an oxime, m. 76°, and a semicarbazone, m. 91°. The portion  $b_{48}$ , 200-7°, which solidifies on cooling, has  $n$  1.534 and m. 82°. It is palmitone, produced from Ca palmitate during dry distn., since its oxime m. 58° and semicarbazone m. 170° C. S. T.

Catalytic oxidation with platinum black. Oxidation of buccocamphor. I. GUNO CUSMANO. *Gazz. chim. ital.* 53, 158-64(1923).—In the course of previously published expts. on hydrogenation of org. compds. C. observed that Pt black frequently favors oxidation at ordinary temps. In this paper results on the oxidation of buccocamphor (I) (Semmler, Mackenzie, *Ber.* 39, 1158(1906)) are described. 5 g. I in a little  $\text{Et}_2\text{O}$  with about 0.5 g. Pt black were placed in a 500-cc. beaker covered with a watch glass and agitated from time to time. The  $\text{Et}_2\text{O}$  was replaced from time to time and after about

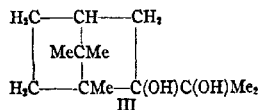
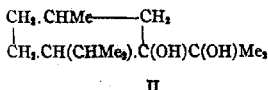
8 days a yellow compd. became abundant. After 15 days the crystals of a compd. (II),  $C_{10}H_{14}O_4$ , m.  $126^\circ$ , were filtered off. II at the m. p. loses  $H_2O$  and gives a hydroxy-buccocamphor (III),  $C_{10}H_{14}O_3$ , m.  $75-6^\circ$ . III is pptd. from its NaOH soln. by  $CO_2$ . II at first dissolves in 20% KOH and a salt seps. as needles, which with  $CO_2$  give some III. IV contains the cymene skeleton unchanged. The  $Et_2O$  filtrate from II, filtered from most of the Pt, was shaken out with  $Na_2CO_3$ , and then with KOH, which took up the unchanged buccocamphor (IV) and some acids. This soln., satd. with  $CO_2$ , gave IV as crystals and a brown oil. contg. IV and III. The brown soln., treated with dil.  $H_2SO_4$  drop by drop, yielded a little hydroxythymoquinone. After filtration excess  $H_2SO_4$  was added and the soln. extd. with  $Et_2O$ , which gave needles of a monobasic acid,  $C_{10}H_{14}O_4$  (V), of which the  $NH_4$ , Ag and Ba salts were obtained. 1 g. V with 5 g.  $PbO_2$  and a little  $H_2O$  were heated on a  $H_2O$  bath and treated drop by drop with 25%  $H_2SO_4$ .



The  $CO_2$  evolved was caught in  $Ba(OH)_2$  soln. The flask contents were worked up and gave an acid (VI),  $C_{10}H_{14}O_4$  (S. and M., *l. c.*). V is considered to be  $MeCH(OH)CH_2CH_2CH(CHMe_2)COCO_2H$  from which VI is derived through  $MeCOCH_2CH_2CH(CHMe_2)COCO_2H$ .

E. J. WITZEMANN

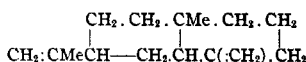
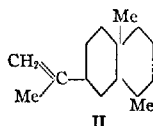
**Chemical action of light.** G. SCAGLIARINI and GIUSEPPINA SALADINI. *Gazz. chim. ital.* 53, 135-39 (1923).—Ciamician and Silber (*Atti accad. Lincei* 22, II, 470) observed that not all org. compds. are attackable by  $O_2$  but that certain autoxidizable compds. can render the  $O_2$  active and cause the nonautoxidizable compd. to be oxidized. Sinda (*Monatsh.* 33, 1277) and Benrath and Meyer (*C. A.* 7, 352) obtained interesting results on the reciprocal influence of org. compds. on autoxidation in light. They obtained from phenanthrenequinone that is not autoxidizable ( $C_{14}H_8O_2$ ) in the presence of PhMe and of xylenes. S. and S. studied the behavior of autoxidizable fenchone and pinene (which alone do not undergo autoxidation) and detd. the products formed through the action of PhMe +  $O_2$  and with pinene with  $H_2C_2O_4$  +  $O_2$ . 4.7 g. fenchone + 4 g. PhMe in 100 cc.  $H_2O$  were placed in 5-l. flasks full of  $O_2$  and isolated nearly 1 year. Much  $CO_2$  was present and 9.3 g. BzOH were sepd. from 8 flasks as well as some AcOH. Similar expts. with 4.7 g. fenchone + 12 g. EtOH in 100 cc.  $H_2O$  gave much  $CO_2$ , an undetd. compd. with 49.39% C and 11.32% H, considerable AcOH and some  $H_2C_2O_4$ . Neither fenchone nor EtOH is oxidized alone; they may form an easily oxidized addn. product but S. and S. could not detect it. Similar expts. with 4.5 g. pinene + 3 g.  $H_2C_2O_4$  in 100 cc.  $H_2O$  gave  $CO_2$ , tar, much unchanged pinene and  $H_2C_2O_4$  and some AcOH. The action of light on mixts. of  $Me_2CO$  with some terpene alcs. was studied to det. if besides the pinacols other more complex condensation products are also formed. The formation of pinacols was confirmed but no more complicated derivs. were obtained. Terpinol hydrate does not condense with  $Me_2CO$ . 79.7 g.  $Me_2CO$  + 53 g. geraniol isolated in a tube for 13 months gave 63 g.  $Me_2CO$ , 32 g. geraniol and a yellowish residuc,  $b_p$   $208-10^\circ$ , composed of  $Me_2C:CHCH_2CH_2$ .



$CMe:CHCH(OH)C(OH)Me_2$  (I) ( $Me_2CO$  has entered into the right end of the geraniol mol.). In a similar mixt. of  $Me_2CO$  and menthol were recovered about 90% of the compds. used and the condensation product II. With borneol and  $Me_2CO$  the most of the compds. used was recovered together with the product III. E. J. WITZEMANN

**Higher terpene derivatives.** VI. The two methylisopropynaphthalenes obtained from cadalene. L. RUZICKA and M. MINGAZZINI. *Helvetica Chim. Acta* 5, 710-5 (1922); cf. C. A. 16, 3893.—6,4,1-Me( $Me_2CH$ ) $C_{10}H_7CO_2H$ , prepd. by oxidation of cadalene with  $CrO_3$ , distd. with  $Ca(OH)_2$ , yields 6-methyl-4-isopropynaphthalene,  $b_p$   $139-41^\circ$ ,  $d_4^{20}$  0.9833,  $n_D^{20}$  1.5894; *pirale*, orange-yellow, m.  $101-2^\circ$ ; *styphnate*, yellow, m.  $163-4^\circ$ . Et  $\beta$ -[1-methyl-4-isopropylphenyl]-2-ethylmalonate,  $b_p$   $200-10^\circ$ ;  $\gamma$ -[1-Methyl-4-isopropylphenyl]-2-butyric acid,  $b_p$   $195-6^\circ$ ; the chloride,  $b_p$   $165^\circ$ ; with  $AlCl_3$  this yields 1-methyl-4-isopropyl-5-ketotetrahydronaphthalene,  $b_p$   $160-70^\circ$ , the semicarbazone of which m.  $178-80^\circ$ . Reduction with Zn-Hg and 20% HCl gives 1-methyl-4-

*isopropyl-5,6,7,8-tetrahydronaphthalene*,  $b_{11}$  135–40°, heated with S at 180–230°, yields *1-methyl-4-isopropyl-5-methylnaphthalene*,  $b_{11}$  135–45°, the *picrate* of which is orange-yellow and m. 99–100°. VII. Constitution of eudalene, selinene and  $\alpha$ -santalene. The carbon framework of the sesquiterpenes. L. RUZICKA AND M. STOLL. *Ibid* 923–36(1922).—Eudalene is shown by synthesis to be *3-isopropyl-5-methylnaphthalene* (I). *Et p-isopropylcinnamate*, from cuminol,  $\text{BrCH}_2\text{CO}_2\text{Et}$  and Zn,  $b_{11}$  167–9°. Reduction with Na and EtOH, yields *p-isopropylhydrocinnamic alc.*,  $b_{11}$  149°. The *bromide*,  $b_{11}$  142°, treated with KCN, sapond. with EtOH-KOH and acidified with HCl gives *p-cumyl-butyric acid*,  $b_{11}$  186° m. 31–2°. *Chloride*,  $b_{11}$  156°.  $\text{AlCl}_3$  transforms this into *3-isopropyl-5-keto-5,6,7,8-tetrahydronaphthalene*,  $b_{11}$  156°; *semicarbazone*, m. 195°. The ketone with  $\text{MeMgI}$  gives *3-isopropyl-5-methyl-7,8-dihydronaphthalene*,  $b_{11}$  137°, which is finally heated at 180–230° with S and then distd. *in vacuo*, giving I. The *picrate*, m. 92°, is identical with that of eudalene. With  $\text{HNO}_3$ , I gives *1,7-naphthalenedicarboxylic acid*, amorphous flakes, m. about 265°, differentiated from the other isomeric acids by its ready soly. in the usual solvents. It is also obtained by the oxidation of  $4,6\text{-C}_{10}\text{H}_4(\text{CHMe}_2)_2$ ; a 2nd oxidation product of this compd. is a *nitro-4-isopropyl-6-methylnaphthalene*, yellow, m. 112–3°, which is further oxidized in the same reaction to a *nitro-4-isopropyl-6-naphthoic acid*, m. 225–7°. From these facts R. and S. propose the following formulas for  $\alpha$ -selinene (II) and  $\beta$ -selinene (III):



C. J. WEST

**Abietic acid.** A. W. SCHORGER. *J. Am. Chem. Soc.* **45**, 1339–40(1923).—"Gum" rosin which had been heated 30 min. at 220–5° under 25 mm., was dissolved in petroleum naphtha (dried with  $\text{CaCl}_2$ ), inoculated with abietic acid and allowed to stand in a cool place; in a week the walls of the vessel were covered with crystals. Rosin which had been distd. *in vacuo* behaved in the same way. Clear lumps of rosin in stoppered bottles contg. distd.  $\text{H}_2\text{O}$  soon became opaque on the surface while in 5 and 20%  $\text{H}_2\text{SO}_4$  they remained perfectly transparent for 7 months. S. therefore does not agree with Steele (*C. A.* **16**, 2324) who, with Knecht and Hibbert, believes that rosin consists mainly of abietic anhydride and not of the acid.

C. A. R.

The utilization of *p*-dichlorobenzene for synthesis in the diphenic acid series. E. B. HUNN. *J. Am. Chem. Soc.* **45**, 1024–30(1923).— $p\text{-C}_6\text{H}_4\text{Cl}_2$  was nitrated to  $2,5\text{-Cl}_2\text{C}_6\text{H}_3\text{NO}_2$  which with aq.  $\text{NH}_3$  at 180° gave 94%  $4,2\text{-Cl}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{NH}_2$ ; this, by the Sandmeyer method, yielded 70–80%  $4,2\text{-Cl}(\text{O}_2\text{N})\text{C}_6\text{H}_3\text{CN}$  (I), m. 97°, which on hydrolysis with hot 70%  $\text{H}_2\text{SO}_4$  gave 93–5% of the acid (II), m. 139°. Attempts to reduce I to the  $\text{NH}_2$  compd. with Fe and AcOH led to the formation of *2-amino-4-chlorobenzamide*, m. 181.5° (cor.), hydrolyzed by boiling 50%  $\text{H}_2\text{SO}_4$  to the acid, m. 240° (cor.) (also obtained in 95% yield from II with  $\text{NH}_4\text{OH}\cdot\text{FeSO}_4$ , whose *Bz deriv.* m. 223.5° (cor.) and *Me ester* m. 68.5°. The diazotized acid with  $\text{NH}_4\text{OH}\cdot\text{CuOH}$  gave 84% of *5,5-dichlorodiphenic acid*, straw-colored, m. 297°, converted by refluxing with  $\text{Ac}_2\text{O}$  into the *anhydride*, m. 206° (cor.) (yield, 95%), insol. in cold but slowly sol. in boiling NaOH.

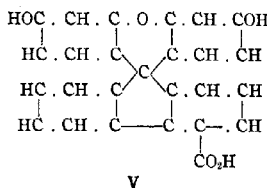
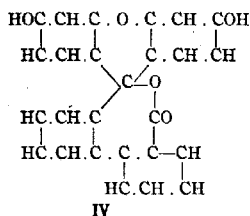
C. A. R.

**Molecular configuration of polynuclear aromatic compounds. II. 4,6,4'-Trinitrodiphenic acid and its resolution into optically active compounds.** G. H. CHRISTIE AND JAMES KENNER. *J. Chem. Soc.* **123**, 779–85(1923); cf. *C. A.* **15**, 2434; **16**, 2136.—*d*-4,6,4',6'-Tetranitrodiphenic acid, contg.  $3\text{H}_2\text{O}$ , m. 53–4°, and then 226–7°; a 1.64% aq. Na salt soln. showed  $[\alpha]_D^{25}$  115°. The *l*-acid also contains  $3\text{H}_2\text{O}$ , m. 52–3°, then 226°; a 1.24% aq. soln. of the Na salt showed  $[\alpha]_D^{25}$  –116°. The action of  $\text{HNO}_3$  upon 2,7-dinitrophenanthraquinone gave the *2,4,7-trinitro deriv.* (in place of the tetranitro deriv. expected), yellow, m. 203°, crysts. with 1 mol.  $\text{C}_6\text{H}_5$  with the same m. p., but the compd. with  $\text{C}_6\text{H}_4\text{Me}_2$  1st m. 125°, then 202–3°. Oxidized with  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ , *dl*-4,6,4'-trinitrodiphenic acid, m. 289°, is obtained; all derivs. were oily. Further oxidation gave the tetranitro acid. *Brucine d*-4,6,4'-trinitrodiphenate, m. 239–40° (decompn.), sol. in 1700 parts cold  $\text{H}_2\text{O}$ ,  $[\alpha]_D^{25}$  –20.79° (1% in 10 *N* AcOH). *Quinidine salt*, m. 229° (decompn.),  $[\alpha]_D^{25}$  –191.1°. The *l*-salt, m. 176° and showed  $[\alpha]_D^{25}$  56.04° (0.71% in  $\text{CHCl}_3$ ). The *d*-acid, m. 281–2°; a 1.5% aq. Na salt soln. shows  $[\alpha]_D^{25}$

156.8°. The *l*-acid did not solidify; a 0.49% soln. of the Na salt showed  $[\alpha]_D^{15} -130.5^\circ$ .

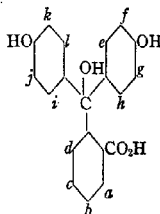
C. J. WEST

**Condensation of diphenic anhydride with resorcinol.** FRITZ BISCHOFF AND HOMER ADKINS. *J. Am. Chem. Soc.* 45, 1030-3 (1923).—Phenanthraquinone, m. 205-7° (cor.), was obtained in 50 g. yield from 100 g. of "80% phenanthrene" oxidized by the Oyster and A. method (C. A. 15, 684). This with  $K_2Cr_2O_7 \cdot H_2SO_4$  gave 85% diphenic acid (I), m. 228°, which by the Graebe and Aubin method yielded 92% of the anhydride (II), m. 219° (cor.). 9,10-Diphenylketone-4-carboxylic acid (III), from I and  $H_2SO_4$  at 130°, m. 217°. II,  $m\text{-}C_6H_4(OH)_2$  and  $ZnCl_2$  at 135-50° yield *o*-[*o*-2,7,9-trihydroxy-xanthhenylphenyl]benzoic *g*-lactone (IV) as a sticky spongy mass obtained in solid form from  $Et_2O$  at 108°, is fluorescent in alkalies and insol. in acids.  $NH_3$  gas changes the yellow IV to a red  $NH_4$  salt with 6.02%  $NH_3$  which reforms IV with  $CO_2$ ; Na salt, brown slimy ppt. with 15.9% Na; *Ac* deriv., yellow, insol. in alkalies; 1,3,6,8-*Br*<sub>4</sub> deriv., from IV and Br in alc., pinkish yellow, dyes silk and wool pink from a faintly acid bath, dissolves in alkalies with intense purple-red color and forms a semicryst. reddish *Ac* deriv., insol. in alkalies. 2',7'-Dihydroxy-*g*-fluorene-*g*'-xanthene-4-carboxylic acid (V), from III,  $m\text{-}C_6H_4(OH)_2$  and  $ZnCl_2$  at 115-20°, dissolves in alkalies with brownish yellow color and green fluorescence; the *Ac* deriv. is sol. in alkalies.



C. A. R.

**Color and chemical constitution. XV.** A systematic study of fluorescein and resorcinolbenzein. JAMES MOIR. *Trans. Roy. Soc. S. Africa* 10, 159-64 (1922); cf. C. A. 16, 2996.—The quant. study of the color of compds. of the phenolphthalein type has been continued. The results previously recorded for the bromophenolphthaleins (C. A. 15, 4004) are restated in another form. The different positions open to substitution in the phenolphthalein mol. are lettered as shown. The color modification due to the introduction of Br into any particular position can be expressed by a factor, the "dicyclic color factor," by which the characteristic wave length of phenolphthalein must be multiplied to give that of the deriv. These factors, for the resp. positions, are: *a* and *d*, 1.018; *b*, 1.002; *c*, *f*, and *g*, 1.0145; *e* and *h*, 1.0270; *i* and *l*, 1.0235; *j* and *k*, 1.0125. If two or more positions are substituted, all the corresponding factors must be used in calcg. the color of the deriv. The color factors for Cl and I are, resp., about  $1/1000$  smaller and greater than those for Br. Similar factors have been worked out for various substituents in fluorescein,  $\lambda = 493.5$ . For Br, the factors for the different positions are: *a* and *d*, 1.0162; *b*, 1.0000; *c*, 1.0091; *f* and *k*, 1.0122; *g* and *j*, 1.0157. The factors for  $NO_2$  derivs. are very similar to those for Br derivs., the Me factors are smaller and the MeO factors smaller still, the largest being 1.006. The HO factors are smallest of all, and in NaOH the HO derivs. have their absorption bands in the same position as fluorescein itself. Gallein and hydroxyquinolphthalein are exceptions to this rule. Resorcinolbenzein, which is fluorescein without the  $CO_2H$  group, is practically identical with fluorescein in alk. soln.; the absorption band is at  $\lambda 492$ . A few derivs. which have been examd. show that the color factors for the *f*, *g*, *i*, and *k* positions are the same as those of phenolphthalein. In the Ph ring the effect diminishes in the order *d*, *c*, *b*, but is still positive for *b*, although in fluorescein it appears to be nil for this position.



J. C. S.

**A new method of preparing dibenzoyl ethylene and related compounds.** J. B. CONANT AND R. E. LUTZ. *J. Am. Chem. Soc.* 45, 1303-7 (1923).— $BeCH_3 \cdot CHBr_2$  (I) and related compds. have been prepd. by adding fumaryl chloride slowly to a mixt. of  $AlCl_3$  and the appropriate hydrocarbon or its deriv. In every case the yellow *trans*-

isomer is formed and can be converted into the colorless *cis*-isomer by the action of sunlight on the appropriate soln. The reverse transformation can be effected by heating the soln. of the colorless isomer with a little HCl or letting it stand with a trace of I for some time. Both isomers are rapidly reduced to the ethane in hot alc. by aq.  $\text{Na}_2\text{S}_2\text{O}_4$ . I is obtained in 74% yield with  $\text{C}_6\text{H}_6$ . *trans*-Diethylstylylene, from PhMe (yield, 75%), m. 148°; *cis*-isomer, m. 123°. *trans*-Di-4-chlorobenzoylstylylene, from PhCl in  $\text{CS}_2$  (yield, 51%), m. 172°; *cis*-isomer, m. 102°; ethane, m. 151°. *trans*-Di-2,4,6-trimethylbenzoylstylylene, from mesitylene in  $\text{CS}_2$  (yield, 75%), m. 174°; *cis*-isomer, m. 120°; ethane, m. 138.5°. Di-4-methoxybenzoylstylylene (obtained in only 1.5 g. yield from 10 g. fumaryl chloride), is vermilion after several crystals from  $\text{Me}_2\text{CO}$  and after exposure to sunlight in  $\text{CHCl}_3$  seps. as a pale yellow solid, m. 165.5°. C. A. R.

An electrochemical method of studying irreversible organic reductions (preliminary paper). J. B. CONANT AND R. E. LUTZ. *J. Am. Chem. Soc.* 45, 1047-60(1923); cf. C. A. 17, 234.—An electrochem. method of studying the irreversible reduction of org. substances in homogeneous soln. has been developed. An upper potential limit for the reduction of certain substances ( $\text{BzCH:CHBz}$ , ( $p\text{-ClC}_6\text{H}_4\text{COCH:}$ )<sub>2</sub>, ( $\text{MeC}_6\text{H}_4\text{COCH:}$ )<sub>2</sub>, (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{COCH:}$ )<sub>2</sub>, PhCBz:CHBz, PhCBz:CHCOCMe<sub>2</sub>, BzCH:CHCO<sub>2</sub>H, BzCH:CHCO<sub>2</sub>Et, Me fumarate, fumaric acid, Bz<sub>2</sub>, PhN:NPh, *sym*-C<sub>6</sub>H<sub>4</sub>(NO)<sub>2</sub>, *m*-C<sub>6</sub>H<sub>4</sub>(NO)<sub>2</sub>, PhNO<sub>2</sub>) under specified conditions in  $\text{Me}_2\text{CO}$ -HCl and in EtOH-HCl has been detd.; this "apparent reduction potential" is in every case except that of Bz<sub>2</sub> essentially the same in the 2 solvents. A theory of irreversible reductions is put forward which connects the "apparent reduction potential" with a true oxidation-reduction potential of the substance in question. The results with the unsatd. C:O compds. show that the potential at which these substances are irreversibly reduced is approx. proportional to the reactivity of the C:O group. The reduction of PhNO to PhNHOH is shown to be reversible and the potential has been measured. C. A. R.

Oxidation of benzeneazaphthols. L. DINO BIGIARI AND RENATO CERCHIARI. *Atti accad. Lincei* [v] 31, ii, 27-30(1922).—Owing to the divergent behavior towards alkali shown by the 3 isomeric benzeneazaphthols, a phenylhydrazonic constitution is attributed to 1-benzeneazo-2-naphthol, while 4-benzeneazo-1-naphthol and 2-benzeneazo-1-naphthol are considered to possess the ordinary hydroxylic formulas (Goldschmidt and Brubacher, *Ber.* 24, 2300-17(1891); Willstätter and Parnas, *C. A.* 1, 1705). Marked differences are found also in the behavior of these compds. towards 30%  $\text{H}_2\text{O}_2$  and AcOH. Thus, under these conditions, 1-benzeneazo-2-naphthol and also its Ac deriv. undergo slow oxidation in the cold to  $\text{HO}_2\text{CCCH}_2\text{CH:CHCO}_2\text{H}$  (I), m. 200°, while in the hot they yield the isomeric dihydroisocoumarincarboxylic acid,  $\text{HO}_2\text{CCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$ , m. 153°, which is also obtained when I is fused for a few

moments. Similar oxidation of  $\beta$ -naphthol yields the products obtained by Ehrlich by the action of  $\text{KMnO}_4$  (*Monatsh.* 10, 115-22(1889)), viz.: (1) I, for which, however, he gave m. 183° instead of 200°; (2) an acid,  $\text{C}_{10}\text{H}_8\text{O}_4$ , m. 281°, which, although regarded by E. as dibasic, gives only mono-Ag and -Et derivs., and has probably the

structure  $\begin{array}{c} \text{CO}_2\text{H} \quad \text{CO}_2\text{O} \\ | \quad | \\ \text{C}_6\text{H}_4\text{CH:} \text{C} \text{---} \text{C}_6\text{H}_4 \end{array}$ . This acid reduces  $\text{KMnO}_4$ , but not so rapidly as does I. J. C. S.

New salts of pyrrole. C. GASTALDI AND G. L. PEYRETTI. *Gazz. chim. ital.* 53, 11-5(1923).—In a previous paper G. (*C. A.* 16, 2515) showed that MeCOPh and dypnone react with  $\text{Ac}_2\text{O}$  +  $\text{FeCl}_3$ , giving the  $\text{FeCl}_3$  salt of 2-methyl-4,6-diphenylpyrrole chloride. G. and P. have now obtained the same reaction with propionic, butyric and isovaleric anhydrides which give  $\text{CH:CPh.CH:CPh.O(FeCl}_3\text{):CR}$  (I), in which R =

Et, Pr or  $\text{CH}_2\text{CHMe}_2$ . 7 g. MeCOPh + 7 g. (EtCO)<sub>2</sub>O when treated gradually with 5 g. sublimed  $\text{FeCl}_3$  and heated an hr. solidified. The product was washed with glacial AcOH and gave the  $\text{FeCl}_3$  salt of 2-ethyl-4,6-diphenylpyrrole chloride (II), yellow, m. 166-7°. II treated with excess  $\text{NH}_4\text{OH}$  sepd., besides  $\text{Fe(OH)}_3$ , 2-ethyl-4,6-diphenylpyridine, which was purified as the nitrate,  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_2$ , m. 180° (decompn.). Aq. II with  $\text{HNO}_3$  ppts. 2-ethyl-4,6-diphenylpyrrole nitrate, yellow, m. 151° (decompn.). 6 g. dypnone + 7 g. (EtCO)<sub>2</sub>O treated as above gave II also. 10 g. MeCOPh + 10 g. (PrCO)<sub>2</sub>O + 8 g.  $\text{FeCl}_3$  treated as above gave the  $\text{FeCl}_3$  salt of 2-propyl-4,6-diphenylpyrrole chloride (III), greenish yellow, m. 197-8°. III with  $\text{NH}_4\text{OH}$  gave 2-propyl-4,6-diphenylpyridine of which the nitrate m. 138° (decompn.). The same products were obtained from dypnone. With (iso-BuCO)<sub>2</sub>O MeCOPh gives the  $\text{FeCl}_3$  salt of 2-isobutyl-4,6-diphenylpyrrole chloride (IV), yellow, m. 165°. IV with  $\text{NH}_4\text{OH}$  gives 2-isobutyl-4,6-diphenylpyridine, of which the nitrate, m. 124°. With  $\text{HNO}_3$  IV gives 2-isobutyl-4,6-diphenylpyrrole ni-

trate (V), yellow, m. 156°. IV and V were obtained similarly from dypnone.

E. J. WITZEMANN

**Nitropyrroles.** ANGELO ANGELI. *Atti accad. Lincei* [v] 31, ii, 3-5 (1922).—Fischer and Zerweck (C. A. 17, 106) state inaccurately that the nitration of alkylpyrroles may be effected smoothly by means of  $\text{HNO}_3$  (cf. Angeli and Alessandri, C. A. 5, 3403). The compds. investigated by these authors are not alkylpyrroles, but esters of  $\text{CO}_2\text{H}$  acids derived from keto-, formyl-, etc., derivs. of pyrrole, and the action on them of  $\text{HNO}_3$  consists, not in true nitration, but in replacement of Ac, aldehydo-, Me, etc., groups by  $\text{NO}_2$  groups.

J. C. S.

**The influence of solvents on the Grignard reaction.** RIKO MAJIMA AND MUNIO KOTAKE. *Rept. Inst. Phys. Chem. Research* (Japan) 2, 82-91 (1923); *J. Chem. Soc. Japan* 43, No. 12 (1922).—The influence of solvents ( $\text{Et}_2\text{O}$  and anisole) on indole-Mg iodide in the Grignard reaction has been studied; the products and the % yields in  $\text{Et}_2\text{O}$  and anisole, resp., were as follows: (0) With  $\text{HCO}_2\text{Et}$ ,  $\beta$ -indole-aldehyde, trace, 33; (1)  $\text{CO}_2\text{H}$ ,  $\beta$ -indolecarboxylic acid, 8.6, 25; (2)  $\text{Me}_2\text{O}$ ,  $\beta, \beta'$ -diindolyl dimethylmethane, 22.5, 30.4; (3)  $\text{BzH}$ ,  $\beta, \beta'$ -diindolyl phenylmethane, 20 (crude), 61.6 (crude); (4)  $\text{ClCO}_2\text{Et}$ ,  $\text{Et}$ - $\beta$ -indolecarboxylate 53.5, 36.7; (5)  $\text{AcCl}$ ,  $\beta$ -acetylindole, 93, 61; (6)  $\text{ClCH}_2\text{COCl}$ ,  $\beta$ -chloroacetylindole, 45 (crude), 4.8. M. and K. conclude that when a compd. having a C:O group acts on  $\text{C}_8\text{H}_7\text{NMgI}$ , good yields are obtained by using anisole as a solvent; when the reacting compd. is an acid chloride,  $\text{Et}_2\text{O}$  is a better solvent. References to earlier work on the above reactions are given.  $\beta$ -Chloroacetylindole, m. 212-4°.

K. KASHIMA

**Isosindigotin and indin.** A. WAHL AND W. HANSEN. *Compt. rend.* 176, 1070-2 (1923).—A study of the reduction products of isosindigotin (C. A. 3, 2143, 2677) and of indin (*Ann. chim. phys.* 3, 471 (1840)) and of the Ag, Ba, K, and Na salts of their disulfonic acids, showed that these products were identical, but not the same as the indin-disulfonic acid derived by Schlieper (*Ann.* 120, 24) from isatinsulfonic acid.

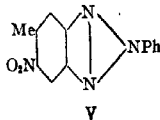
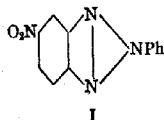
T. S. CALSWELL

**Reactions of thiosemicarbazones. II. Action of esters of  $\alpha$ -halogenated acids.** F. J. WILSON AND ROBERT BURNS. *J. Chem. Soc.* 123, 799-804 (1923); cf. C. A. 16, 2481.— $\text{Me}_2\text{C}:\text{N}:\text{C}(\text{SNH})\text{NH}_2$  and  $\text{MeCHBrCO}_2\text{Et}$  in  $\text{EtOH}$  give 2,4-diketo-5-methyl-tetrahydrothiazole-2-isopropylidenehydrazone,  $\text{Me}_2\text{C}:\text{N}:\text{C}(\text{NH})\text{CO}.\text{CHMe}.$  S, m. 150°;

if this is hydrolyzed with concd.  $\text{HCl}$ ,  $\text{Me}_2\text{CO}$  and  $\text{N}_2\text{H}_4$  are split off, giving 2,4-diketo-5-methyltetrahydrothiazole, but if 2 *N*  $\text{HCl}$  is used,  $\text{Me}_2\text{CO}$  only is removed, giving 2,4-diketo-5-methyltetrahydrothiazole-2-hydrazone hydrochloride, decomps. above 220°, slightly hygroscopic, reduces Fehling soln. Benzylidene deriv., m. 236°. 2,4-Diketo-5-ethyltetrahydrothiazole-2-isopropylidenehydrazone, m. 116°, gives with 2 *N*  $\text{HCl}$  as above the 2-hydrazone hydrochloride, decomp. 215-20°; benzylidene deriv., m. 206°. The free hydrazone, m. 139° is liberated from the aq. soln. of the  $\text{HCl}$  salt by  $\text{Na}_2\text{CO}_3$ . 2,4-Diketo-5-phenyltetrahydrothiazole-2-isopropylidenehydrazone, m. 198-9°. The corresponding 2-hydrazone hydrochloride decomps. above 240°; benzylidene deriv., m. 257°. The free hydrazone could not be prepd.

C. J. WEST

**Some o-nitrohydrazo compounds.** MICHELE GIUA AND MARIO GIUA. *Gazz. chim. ital.* 53, 165-74 (1923).—In a previous paper (C. A. 13, 841) it was shown that  $\text{HCl}$  gas acting on o-nitrohydrazo compds. in  $\text{MeOH}$  or  $\text{EtOH}$  gives a wine-red coloration. The reaction is quite general and serves to identify the products of  $\text{PhNHNH}_2$ , acting on aromatic  $\text{NO}_2$  compds. contg. labile Cl, Br, alkoxy,  $\text{NO}_2$ , etc. o-Nitrohydrazo compds. are the primary products but the above compds. also react, giving benzotriazole or phenylazimidobenzene derivs. Thus from  $\text{PhNHNH}_2$  and 2,4-( $\text{O}_2\text{N}$ ) $_2$ - $\text{C}_6\text{H}_3\text{Br}$ , Kehrman and Messinger (*Ber.* 25, 838 (1892)) obtained phenylpseudoazimidido-6-nitrobenzene (I), which is isomeric with dinitrosoazobenzene. In a previous paper G. (C. A. 14, 1530) described a compd. as dimethyldinitrosoazobenzene which



is really phenylpseudoazimidido-1,4-dimethyl-5-nitrobenzene. Similarly methyldinitrosoazobenzene is one of 2 possible isomers derived from the nucleus of I. At that time

it was known that these compds. do not behave like nitroso derivs. —(RN:N)CC(NO)— but like azimidoxides, —N.N.N:O, or azinitroso derivs., —N.N.N.O—. The above

color reaction with HCl serves to det. whether the *o*-nitrohydrazo compd. (II) or a phenylazimidobenzene deriv. (III) was obtained since in alc. II gives the red color with HCl gas while III does not. The reaction of Werner and Stiasny (*Ber.* 32, 3257(1899)) and of Willgerodt (*J. prakt. chem.* 55, 382(1897)) do not permit of adequate distinction as between II and III. The action of HCl on II is not easy to det. and is discussed. One interpretation was fully studied by Jacobson (*C. A.* 16, 2318), who found that part of the hydrazo compd. reacts with HCl, giving the corresponding azo compd. while the 2 H atoms split another mol. of the hydrazo compd. giving 2 mols. of a primary amine. II can in part undergo this reaction with the formation of a nitrosoazo compd. to which the HCl can add to the azo group, giving the red compd. The azimidoxide also formed does not give a red color with HCl. In expts. with alc. 5,2,4-Me(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N:NPh and HCl gas the red color appeared and disappeared on adding H<sub>2</sub>O, by which the unchanged azo compd. was pptd. This showed that part was converted into a deriv. of III and some into II; this was converted into a nitrosoazo compd. which is red in the presence of an inorg. acid. 5,2,4-Me(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNHPh (IV) in EtOH (*C. A.* 13, 841) treated drop by drop with 15% NaOH sepd. *phenylpseudoazimido-6,5-methylnitrobenzene N-oxide* (V), yellow, m. 155–6°. IV in EtOH with HCl gas gives V also as well as some of the Me(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N:NPh. IV in EtOH boiled 0.5 hr. with HgO gave, after filtering and cooling, 2,4-dinitro-5-methylazobenzene, red, m. 117–8°. 5,2,6-Me(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNHPh treated with HgO gave the corresponding *azobenzene deriv.*, red-yellow, m. 148–9°.  $\gamma$ -MeC<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> with *o*-MeC<sub>6</sub>H<sub>4</sub>NHNH<sub>2</sub> gave 2,4-dinitro-5,2'-dimethylhydrazobenzene (VI), orange-red plates, m. 151–2° (decompn.). VI in hot EtOH with 25% KOH or with HCl gas gave *o*-tolylpseudoazimido-6,5-methylnitrobenzene N-oxide, yellow, m. 142–3°.  $\gamma$ -MeC<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> with *m*-C<sub>6</sub>H<sub>4</sub>NHNH<sub>2</sub> gave 2,4-dinitro-5,3'-dimethylhydrazobenzene (VII), orange-yellow, m. 165–6°. VII treated in EtOH with 25% KOH or boiled with glacial AcOH gave *m*-tolylpseudoazimido-6,5-methylnitrobenzene N-oxide, yellow, m. 181–2°.  $\gamma$ -MeC<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub> with *m*-MeC<sub>6</sub>H<sub>4</sub>NHNH<sub>2</sub> in EtOH boiled for 2 hrs. gave *m*-tolylpseudoazimido-6,5-methylnitrobenzene N-oxide, golden prisms, m. 156–1°. 2,4-Dinitro-5,4'-dimethylhydrazobenzene (*C. A.* 16, 2680) in EtOH with HCl gas gave *p*-tolylpseudoazimido-6,5-methylnitrobenzene N-oxide, green-yellow, m. 188–7°. 5,2,4-Cl(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNHPh with HCl gave *phenylpseudoazimido-6,5-chloronitrobenzene N-oxide*, golden needles, m. 195–6°.

E. J. WITZGERMANN

Ring closure of hydrazodithio- and -monothiodicarboxamides with acetic acid. P. C. GURA. *J. Am. Chem. Soc.* 45, 1036–42(1923).—(NHCSNH<sub>2</sub>)<sub>2</sub> and its mono- and disubstituted alkyl and aryl derivs. react with Ac<sub>2</sub>O according to the equation (NH-CSNH<sub>2</sub>)<sub>2</sub> → [NHC(:NH)SH]<sub>2</sub> → HN:C.NAc.NAc.C(:NH).S (I) or

AcNHC:N.N:C(NHAc).S + H<sub>2</sub>S, and the monothio compds. according to the equation H<sub>2</sub>NCSNHNHCONH<sub>2</sub> → HSC(:NH)NHNHCONH<sub>2</sub> → HN:C.NH.NH.CO.S

(II) + NH<sub>3</sub>. 3,4-Diacetyl-2,5-dimino-2,3,4,5-tetrahydro-1,3,4-thiadiazole (I) (about 4 g. from 5 g. (NHCSNH<sub>2</sub>)<sub>2</sub>), m. above 315°, is insol. in alkali; 3 g. boiled with HCl (d. 1.16) gives 1.4 g. of the HCl salt, C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>S.HCl.H<sub>2</sub>O, m. 241°, of *diminotetrahydrothiadiazole* (III), m. 210–1°, which gives with HNO<sub>3</sub> a chocolate-colored ppt. sol. in alkali with deep red color and forms a yellow *picrate*, darkens 250°, does not m. 265°. 2,5-Me<sub>2</sub> deriv. of I (3.5 g. from 4 g. of (NHCSNHMe)<sub>2</sub>), m. 219°. *Di-Me deriv.* of III, m. 180°; *HCl salt* (1H<sub>2</sub>O), m. 235°; *NO deriv.*, C<sub>6</sub>H<sub>7</sub>(NO)N<sub>2</sub>S, golden yellow, m. 151°; *picrate*, yellow, m. 205°. *Diallyl deriv.* of I, m. 113°. *Diallyl deriv.* of III, m. 151°; *HCl salt* (1H<sub>2</sub>O). *Di-Ph deriv.* of I, m. 224°, hydrolyzed by boiling concd. HCl to the *di-Ph deriv.* of III, m. 247°. *Di-p-tolyl deriv.* of I, m. 235°; of III, m. 249–50°. *Mono-Ph deriv.* of I, m. 144°. *Ph deriv.* of III, dull yellow, m. 215°; *HCl salt* (1H<sub>2</sub>O), m. 144°; *picrate*, yellow, m. 226°. *Di-p-bromophenylhydrazodithiodicarboxamide*, from NaH<sub>2</sub>.H<sub>2</sub>SO<sub>4</sub>, 1 mol. Na<sub>2</sub>CO<sub>3</sub> and 2 mols. BrC<sub>6</sub>H<sub>4</sub>NCS refluxed in aq. alc., m. 213°. *Di-p-bromophenyl deriv.* of I, m. 229°; of III, m. 241°. *Di-m-chlorophenylhydrazodithiodicarboxamide*, m. 170°. *Di-m-chlorophenyl deriv.* of III (that of I could not be isolated pure), m. 186–7°. *Di- $\alpha$ -naphthylhydrazodithiodicarboxamide*, shrinks 235°, m. 265°. *Di- $\alpha$ -naphthyl deriv.* of I, m. 270°; of III, m. 275–6°. *Ac deriv.* of II, m. 295°, hydrolyzed by HCl to the *HCl salt*, m. 107–8°, of 2-*keto-5-iminotetrahydrothiadiazole* (II), m. 240°, insol. in alkali.

C. A. R.

Glucoside occurring in the timber of the "red ash," *Alphitonia excelsa*, Reiss. H.

GRO. SMITH AND JOHN READ. *J. Proc. Roy. Soc. N. S. Wales* 56, 253-9(1923).—In its general phys. and chem. behavior, this secretion of *A. excelsa* shows a marked resemblance to fustin, a glucoside of fisetin, m. 218-9°, first isolated by Schmid (*Ber.* 19, 1734), the latter compd. having been characterized many years previously by Chevreul (Leçons de chimie appliquées à la teinture, A. II, p. 150). Fisetin was later shown by A. G. Perkin (*J. Chem. Soc.* 71, 1194(1897)) to occur in the wood of *Rhodospheera rodanthema*, both free and combined as the supposed glucoside, m. 215-7° and having the formula  $C_{20}H_{20}O_{16}$ . Owing to its unusual resistance to hydrolysis, the complete diagnosis of this compd. has been attended with considerable difficulty, and some doubt still exists concerning the identity of the compd. from *R. rodanthema*, m. 215-7°, with the fustin from *Rhus cotinus* (cf. Schmid, *l. c.*), m. 218-9°, although Perkin and Everest (*The Natural Organic Coloring Matters* (C. A. 13, 662)) have more recently entertained the possibility that these substances are identical. Since it was surmised by Schmid that fustin yielded rhamnose on hydrolysis, Perkin suggested the formula  $C_{20}H_{20}O_{14}$  for the compd. The secretion or deposit isolated from *A. excelsa* yields on extrn. and crystn. from  $H_2O$  an almost colorless powder, m. 218-9° (decompn.), darkening at about 200°; it is pptd. by  $Pb(OAc)_2$ ,  $SnCl_4$  and  $Cu(OAc)_2$ , reduced by Fehling soln. and  $NH_4AgNO_3$  upon heating, colored green by  $FeCl_3$ , this color changing through blue-purple to red on addn. of  $NaOH$ . These color changes together with the other reactions enumerated indicate that the compd. is phenolic in character, having 2 OH groups arranged in the mol. in the *o*-position, similar to catechol. The absence of methylated phenolic groups is shown. The substance possesses dyeing properties when applied to mordanted cloth. When boiled for 15 hrs. with dil.  $H_2SO_4$ , very little hydrolysis occurs. The small amt. of sugar isolated yielded a somewhat impure osazone, m. 188-90°. On heating at 150° for 3 hrs. the glucoside suffered a loss in wt. corresponding closely to 3 mols. of  $H_2O$ , calcd. from the formula  $C_{20}H_{20}O_{14}$ . It yields the cryst. *K* salt,  $C_{20}H_{18}O_{14}K_2$ , as well as a corresponding *NH\_4* salt. The exptl. evidence appears to indicate that the glucoside mol. contains 2 fisetin nuclei united with 1 sugar nucleus, and that only 1 phenolic group in each fisetin residue is effective in giving rise to metallic derivs. Acetylation of the glucoside yields a cryst. compd. which may be a *hexa-Ac derivs.*

W. O. E.

**Direct synthesis of certain xanthylum derivatives.** D. D. PRATT AND ROBERT ROBINSON. *J. Chem. Soc.* 123, 739-45(1923).—When a moderate stream of  $HCl$  is passed through 1,3,5- $C_6H_3(OH)_3$  in  $HCO_2Et$  for 20 min. a quant. yield of 1,3,6,8-tetrahydroxyxanthylum chloride (I),  $C_{12}H_8O_4Cl \cdot H_2O$ , yellow, is obtained; it darkens at 100° because of loss of  $H_2O$ , turns dark brown at 250° but does not decomp. below 330°. The alk. soln. is orange-red. Sulfate, orange-red. Picrate, yellow or red, depending on the concn. of the soln. from which it crystals.  $FeCl_3$  gives a yellow compd., which is probably a double compd. of the  $FeCl_3$  deriv. of the acetate and chloride.  $EtOH-KOAc$  and I give 1,6,8-trihydroxyfluorone, deep red, does not m. 330°. The  $EtOH$  soln. is yellow with green fluorescence.  $HCl$  transforms it into I. 3,6-Dihydroxy-1,8-dimethylxanthylum chloride (II), from orcinol in  $HCO_2Et$  and  $HC(OEt)_2$ , red with green glance, blackens about 280° but does not m. 330°. Glacial  $AcOH$  deposits the acetate, reddish brown with green reflex (individual transparent crystals are orange-yellow), contains 1  $H_2O$  of crystn., darkens 290°, m. 305°. Picrate, golden yellow, decomp. 252°. The  $FeCl_3$  deriv. is probably abnormal and forms yellowish brown prisms with intense peacock blue reflex. Hot aq.  $NaOAc$ , acting upon II, gave 6-hydroxy-1,8-dimethylfluorone, dark red with green reflex, darkens 280°, does not m. 330°. Even the very dil. aq. soln. possesses a vivid green fluorescence. 3,6-Dimethoxy-1,8-dimethylxanthylum ferrichloride, orange-yellow, m. 221°. The  $H_2SO_4$  soln. is yellow with a green fluorescence.  $\beta-C_{10}H_7OH$  reacts in  $HC(OEt)_2$  alone but the yield of chloride is poor. The main product of the reaction is  $C_{10}H_7OEt$ . Dinaphthopyrylium picrate, reddish crimson with a Cu luster, m. 239°. Ferrichloride, orange-brown, m. 288°. The use of other acids than  $HCO_2H$  does not give satisfactory results. Only traces of oxonium salts were obtained from most phenols (quinol, catechol,  $PhOH$  and *m*- $Me-C_6H_4OH$ ).

C. J. WEST

**$\beta$ -Amino- and  $\beta$ -hydroxyquinoline.** G. BARGELLINI AND S. BERLINGOZZI. *Gazz. chim. ital.* 53, 3-11(1923).—Although quinoline derivs. with  $NH_2$  or  $OH$  groups in the  $\alpha$ - or  $\gamma$ -position in the pyridine ring are known, little is known about  $\beta$ -derivs. and no general method for their prepn. exists. Königs and Stockhausen (*Ber.* 35, 2536(1902)) probably obtained  $\alpha$ -methyl- $\beta$ -hydroxyquinoline (I) but the position of the  $OH$  group was never detd.; Baudisch (*C. A.* 13, 297; 16, 2849) obtained I by the same method. B. and B. have now obtained  $\alpha$ -phenyl- $\beta$ -hydroxyquinoline (II) similarly from *o*- $H_2NC_6H_4CHO$  and  $PhCOCH_2Br$ . The fact that  $\alpha$ -[*p*-methoxyphenyl]- $\beta$ -hydroxyquinoline



(III) was also obtained from  $\text{ClCH}_2\text{COC}_6\text{H}_4\text{OMe}$  shows that the action of ketones contg. the group  $-\text{COCH}_2\text{X}$  on  $o\text{-H}_2\text{NC}_6\text{H}_4\text{CHO}$  in the presence of caustic alkali is a general reaction for the prepn. of substituted  $\beta$ -hydroxyquinolines. Mills and Watson (C. A. 4, 2115) obtained  $\beta$ -aminoquinoline from  $\alpha$ -hydroxyquinoline- $\beta$ -carboxylic acid. Stark (C. A. 2, 120) obtained  $\alpha$ -methyl- $\beta$ -aminoquinoline (IV) from  $\alpha$ -methyl- $\beta$ -acetylquinoline. B. and B. obtained IV readily from  $o\text{-H}_2\text{NC}_6\text{H}_4\text{CHO}$  and acetylphthalimide by decomp. the product with HCl. IV with  $\text{HNO}_3$  gives I.  $\alpha$ -Phenyl- $\beta$ -aminoquinoline (V) was obtained similarly, and this with  $\text{HNO}_3$  gives II. Other expts. under way show that this also is a general method. A somewhat similar reaction between metazonic acid,  $\text{HON}:\text{CHCH}_2\text{NO}_2$  and aromatic  $\alpha$ -aminoaldehydes and ketones for the prepn. of  $\beta$ -nitroquinoline derivs. was recently patented (Badische, D.R.P. 335197). 4 g.  $o\text{-O}_2\text{NC}_6\text{H}_4\text{CHO}$  were reduced with  $\text{FeSO}_4 + \text{NH}_4\text{OH}$  (Friedländer, Göring; Ber. 17, 457(1884)), the  $o\text{-H}_2\text{NC}_6\text{H}_4\text{CHO}$  formed distd. with steam and the first 300 cc. of distillate mixed with 5 g. acetylphthalimide (Gödeckemeyer, Ber. 21, 2684(1888)) in 200 cc.  $\text{H}_2\text{O}$ . 200 cc. 30% NaOH were then added. After a few days the liquid was concd. 0.5 on the  $\text{H}_2\text{O}$ -bath. On acidifying with  $\text{AcOH}$   $\text{MeC:N. C}_6\text{H}_4\text{. CH:CNHCOC}_6\text{H}_4\text{CO}_2\text{H}$

(VI) sepd. as a yellowish powder, m.  $220^\circ$  (decompn.), easily sol. in alkali carbonates and reprecip. with  $\text{AcOH}$ . VI + 20% HCl boiled 2 hrs. sepd. phthalic acid on cooling. The filtrate made alk. with  $\text{NH}_4\text{OH}$  seps. IV, bright yellow, m.  $158\text{--}60^\circ$ ; with  $\text{AcOH} + \text{Ac}_2\text{O}$  IV gives the *Ac deriv.*, m.  $164^\circ$ . The *picrate* of IV, yellow, decomp.  $235^\circ$ . IV in dil.  $\text{H}_2\text{SO}_4$  treated as usual with  $\text{NaNO}_2$  soln., boiled 10 mins. to eliminate gas and then cooled and mixed with satd.  $\text{NaOAc}$  sepd. I, yellow, darkens  $280\text{--}40^\circ$ , decomp.  $260^\circ$ . A  $o\text{-H}_2\text{NC}_6\text{H}_4\text{CHO}$  soln. obtained as before was treated with phenacylphthalimide, m.  $167^\circ$ , and treated as with VI. The intermediate product (Me in VI = Ph), m.  $205\text{--}6^\circ$  (decompn.); this heated 2 hrs. with 20% HCl, etc., as with IV, gave V, yellow, m.  $115\text{--}6^\circ$ ; *Ac deriv.* of V, m.  $173\text{--}5^\circ$ ; *picrate*, yellow, m.  $194\text{--}5^\circ$ . V diazotized as with IV gave II, yellow-white, m.  $221\text{--}2^\circ$ . II was also obtained from  $\text{PhCOCH}_2\text{Br}$  as stated above. The *HCl salt* of II, yellowish, m.  $243\text{--}5^\circ$ ; *chloroplatinate*, orange, does not m. below  $260^\circ$ ; *picrate*, yellow, m.  $235\text{--}8^\circ$  (decompn.).  $o\text{-H}_2\text{NC}_6\text{H}_4\text{CHO}$  soln. treated with *p*-chloroacetoanisole and NaOH for 3-4 days at room temp. and then with excess  $\text{CO}_2$  sepd. crude III, purified as the *sulfate*, yellowish, m.  $225\text{--}30^\circ$  (decompn.), which with  $(\text{NH}_4)_2\text{CO}_3$  gave free base, m.  $240\text{--}2^\circ$  (decompn.), insol. in  $\text{H}_2\text{O}$ . The *hydrochloride*, *chloroplatinate* and *picrate* were obtained.

E. J. WITZEMANN

Synthesis of pyrylium salts of anthocyanidin type. II. D. D. PRATT and ROBERT ROBINSON. J. Chem. Soc. 123, 745-58(1923); cf. C. A. 16, 3483.— $\omega$ -Methoxyacetophenone (I), from  $\text{PhMgBr}$  and  $\text{MeOCH}_2\text{CN}$ , b<sub>760</sub>  $118\text{--}20^\circ$ , b<sub>760</sub>  $228\text{--}30^\circ$ , n 1.5416. With 6-aminopiperonal it condenses to methoxymethylenedioxyphenylquinoline, the semicarbazone of which m.  $85^\circ$ . I, condensed with  $o\text{-HOC}_6\text{H}_4\text{CHO}$  and then treated with HCl and  $\text{FeCl}_3$ , gives 3-methoxy-2-phenylbenzopyrylium ferrichloride, golden yellow, m.  $118^\circ$ , which is decompd. by  $\text{H}_2\text{O}$  forming the colorless pseudo-base. The yellow  $\text{H}_2\text{SO}_4$  soln. exhibits pale ivy-green fluorescence. 7-Hydroxy-3-methoxy-2-phenylbenzopyrylium chloride, orange-red, decomp.  $202^\circ$ , is obtained by the action of HCl upon I and  $\beta$ -resorcyraldehyde in glacial  $\text{AcOH}$ ; ferrichloride, red with green luster, m.  $143^\circ$ ; the double thallate chloride,  $3\text{C}_{16}\text{H}_{13}\text{O}_3\text{Cl} \cdot \text{TiCl}_3 \cdot 4\text{H}_2\text{O}$ , brick-red, m.  $144^\circ$ .  $\omega$ ,4-Dimethoxyacetophenone (II), b<sub>85</sub>  $185\text{--}90^\circ$ , m.  $40^\circ$ . Dimethoxymethylenedioxyphenylquinoline semicarbazone, m.  $149^\circ$ . 4-Methoxy-2-hydroxy- $\beta$ -methoxystyryl ketone, by condensing II with  $o\text{-HOC}_6\text{H}_4\text{CHO}$  with  $\text{EtOH-KOH}$ , m.  $160^\circ$ . HCl and  $\text{FeCl}_3$  transform this into 3,4'-dimethoxy-2-phenylbenzopyrylium ferrichloride, orange-red, m.  $135^\circ$ . The concd.  $\text{H}_2\text{SO}_4$  soln. has a vivid jade-green fluorescence. 7-Hydroxy-3,4'-dimethoxy-2-phenylbenzopyrylium chloride, by the action of HCl upon II and  $\beta$ -resorcyraldehyde, intense crimson, decomp.  $218^\circ$ . The color base is obtained as a dark reddish violet ppt. on the addn. of  $\text{AcONa}$  to the chloride in dil. HCl. Excess tap-water gives a bluish red soln., which, if very dil., is decolorized upon standing 0.5 hr. Pseudobase formation evidently depends upon the H-ion concn., the limits between which this may be very being very close together. Ferrichloride, deep red, m.  $162^\circ$ .  $\omega$ -Ethoxyacetoveratrone (?), by the action of  $\text{AlCl}_3$  upon veratrole and  $\text{EtOCH}_2\text{COCl}$  in  $\text{CS}_2$ , b<sub>80</sub>  $245\text{--}50^\circ$ , m.  $68^\circ$ ; it does not yield a semicarbazone and condenses with resorcyraldehyde to give a crimson product which is not a pyrylium salt.  $\omega$ -Chloroacetovanillone, m.  $102^\circ$ ;  $\text{EtOH-FeCl}_3$  gives a green color. Boiled with  $\text{AcOK}$  in  $\text{EtOH}$  for 2 hrs., hydrolyzed and then treated with  $\text{PhNHNH}_2$ , it yields 4-hydroxy-3-methoxyphenylglyoxal diphenylhydrazone,  $\text{HO}(\text{MeO})\text{C}_6\text{H}_3\text{C}(\text{N}_2\text{HPh})\text{CH:N}_2\text{HPh}$ , yellow, m.  $186^\circ$ . The crude *Ac deriv.*, heated with  $o\text{-HOC}_6\text{H}_4\text{CHO}$  and  $\text{MeOH-KOH}$  for 1 hr., and the resulting oil treated with HCl and  $\text{FeCl}_3$ , gave 3,4'-dihydroxy-3'-methoxy-2-phenylbenzopyrylium ferrichloride,

red, m. 142°. The violet color base results upon the addn. of AcONa to the dil. HCl soln. but this is rapidly decolorized in dil. soln. *ω*-Hydroxyacetoveratrone, sirup, was characterized by its *dehydrodiphenylhydrazone*, yellow, m. 164°. The *MeO deriv.*, b<sub>p</sub> 200–5°, gave two *semicarbazones*; a, the less sol., m. 205°, and b, m. 168°. Hydrolysis of either product gave a N-free product. 7-Hydroxy-3,3',4'-trimethoxy-2-phenylbenzopyrylium ferrichloride, red, m. 156°. The corresponding 3,2',4'-deriv., golden-brown, m. 160°. C. J. WEST

A new reaction of the alkaloids and the preparation of the iodostibinates of these substances in the crystalline state. CAILLE AND E. VIRL. *Compt. rend.* 176, 1156–9 (1923).—A yellow amorphous ppt. forms when 1 cc. of a soln. contg. the HCl salt of an alkaloid is added in the cold to 4 cc. of a soln. contg. 5 g. SbCl<sub>3</sub>, 20 cc. concd. HCl and 40 g. KI in 100 cc. H<sub>2</sub>O. The reaction is given with 1 part of quinine in 100,000, and is of the same order of sensitiveness for hordeine, cinchonine, strychnine, emetine, sparteine, pilocarpine, morphine, veratrine, atropine, cocaine, caffeine, theobromine, pyridine, and quinoline. It is given by more concd. solns. of other bases, as PhNH<sub>2</sub>, PhNMe<sub>2</sub>, and MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, but at a diln. of 1:500 only by the alkaloids. By mixing together at 95° an excess of the Sb reagent with such a concn. of the alkaloid that no ppt. was formed, and then allowing the mixt. to cool slowly, the double iodide was obtained in yellow crystals. T. S. CARSWELL

Physostigmine. I. Alkylation products of eseroline. GEORGE BARGER AND EDGAR SYEDMAN. *J. Chem. Soc.* 123, 758–69 (1923); cf. C. A. 15, 2877.—*Eseroline Me ether dimethiodide*, (I), C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>I<sub>2</sub> (incorrectly given as C<sub>10</sub>H<sub>11</sub>ONaI in the 1st paper), probably results according to the equation: C<sub>10</sub>H<sub>10</sub>ON<sub>2</sub>I + 5MeI + 3 EtONa + NaOH = C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>I<sub>2</sub> + 4NaI + 3EtOH. The name *esoline* is given to the phenolic ditertiary base, C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>. The *dimethopchlorate*, m. 294° and decomp. violently when heated on Pt foil. The *Et ether dimethiodide* (II), C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>I<sub>2</sub>, m. 208° (decompn.), is optically inactive. The *dimethopchlorate*, m. 272–3°. *Eseroline ethiodide*, m. 172°. *Eseroline Me ether Me Et diguaternary iodide*, C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>I<sub>2</sub>, decomp. about 212°. The corresponding *Et ether deriv.* m. 201° (decompn.). Heating II with HI for 0.5 hr. splits off EtI, giving *esoline dimethiodide*, m. 212°, which may be converted into I by boiling with Na and MeI. Decompn. of II by Hofmann's method gave Me<sub>2</sub>N and a substance isolated as the *picrate*, C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>N<sub>3</sub>, m. 208–10°. In another expt., a *methiodide*, m. 172° and then solidified and did not m. 270°, which analyzed for C<sub>10</sub>H<sub>10</sub>ON<sub>2</sub>·MeI, was isolated. Boiling II with concd. HNO<sub>3</sub> converts it into a mixt. of the corresponding diguaternary nitrate and *iodoesoline Et ether dimethiodide*, which was purified as the *dimethiodide* (III), yellow, m. 225° (decompn.). HI with III gives *hydroxyesoline dimethiodide*, m. 212° (decompn.), which with EtI and Na gives the corresponding *Et ether*, C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>I<sub>2</sub>, pale yellow, m. 205° (decompn.). *Iodoesoline Me ether dimethiodide*, from HNO<sub>3</sub> and I, pale yellow, m. 237° (decompn.). C. J. WEST  
*Eseretholemethin*, with Na and MeI gave II.

The commercial applications of catalysis in organic chemistry (MAILHE) 13. Simplified method of writing electronic formulas (WILLIAMS) 2. Recent investigations on the composition of wood and lignin (WAHLBERG) 23. Crystallographic study of  $\alpha,\gamma$ -diketohydrindene (PICCHETTO) 2. Chemical reactivity. I. Mechanism of the formation of valerolactone (GARRETT, LEWIS) 2. Freeing propionates from acetates (U. S. pat. 1,450,392) 16.

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ROUX, ULYSSE: *La grande industrie des acides organiques. Technologie complète, commerce, fabrication, calculs et devis d'installation*. 2nd Ed. Edited by Albert Aubry. Paris: Dunod. 147 pp. F. 59.

Polymerization of unsaturated organic acids. H. HAUSMANN and J. LUND. *Can.* 230,458, Apr. 17, 1923. Unsatd. fatty acids free from glycerol are heated under pressure

to 200° with bases. The product so formed is free from the decompn. compds. of other processes. Cf. C. A. 17, 2060.

**Dihydroxyperylene and perylene.** A. ZINKE. U. S. 1,454,204, May 8. Dihydroxyperylene, which may be obtained by the process of U. S. pat. 1,454,205 (below), is used for prepg. perylene by reducing it with a metal such as Zn dust in a current of H at a temp. (preferably about 480-500°) which is above the distg. temp. of perylene. Cf. C. A. 17, 1968.

**Dihydroxyperylene.** A. ZINKE. U. S. 1,454,205, May 8. Dihydroxyperylene is obtained by mixing 2,2'-dimethoxy-1,1'-dinaphthyl or a similar compd. with AlCl<sub>3</sub>, heating the mixt. to a temp. somewhat below the m. p. of dihydroxyperylene (preferably about 140-150°) with exclusion of water and then lixiviating the reaction mixt. with dil. HCl to remove other substances and leave a residue of dihydroxyperylene, which is obtained in almost quantitative yield. Cf. C. A. 16, 721.

**Ethylidene diacetate and similar compounds.** F. W. SKIRROW and J. DICK. U. S. 1,449,918, Mar. 27. Ethylidene diacetate is prepd. by heating vinyl acetate with HOAc in the presence of fuming sulfuric acid, a S oxide or a Hg compd. or other catalyst at a temp. of about 80-90°. A yield of about 85-90% the theoretical amt. may be obtained. The reaction mixt. may be subjected to fractional distn., NaOAc being first added to render H<sub>2</sub>SO<sub>4</sub> inactive if it is used as catalyst. Ethylidene diformate (from vinyl formate) and ethylidene dibutyrate (from vinyl butyrate) may be similarly formed as may also other analogous diesters.

**Chlorinating methane.** E. H. RIESENFELD. U. S. 1,455,508, May 15. In conducting reactions between Cl and CH<sub>4</sub>, sudden stoppage and sudden release of flow of gases to the reaction chamber is prevented by safety devices. A source of actinic light is also provided with safety control devices.

**Rendering ketone chlorides soluble.** A. R. DE VAINS. Can. 230,818, May 8, 1923. Ketone chlorides or other org. products oxidized by the action of Cl on a semi-paste of cellulose are rendered sol. by treatment with alk. lyc which has been used in lixiviating org. material.

**Refining naphthalene chlorides.** K. RÜCKER. U. S. 1,455,509, May 15. Mixts. of C<sub>10</sub>H<sub>7</sub> chlorides adapted to serve as rosin substitutes are refined by passing air or other inert gas through them while molten and at a temp. of 215°.

**Glycol.** W. H. RODERUSH. U. S. 1,454,604, May 8. Glycol diacetate and alc. are heated to about 70-100° in the presence of a catalyst such as H<sub>2</sub>SO<sub>4</sub>, HCl, HOAc or NaHSO<sub>4</sub> in order to form EtOAc and glycol. Glycol propionate or butyrate also may be used similarly to produce glycol.

**Catalytic apparatus for aldehyde manufacture.** E. J. WINTER. U. S. 1,454,609, May 8. Catalytic material such as Cu, Ni, Cr or Fe on pumice is carried within inclined tubes arranged in sets within a furnace and connected to chambers set in the walls of the furnace.

**5(4)-Arylalkylaminoalkylglyoxalines of the general formula C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>[CH<sub>2</sub>]<sub>n</sub>NH-[CH<sub>2</sub>]<sub>m</sub>-Aryl.** OTTO GERNGROSS. Ger. 332,955. Cf. C. A. 9, 694, 1096. Chloroalkylglyoxalines of the general formula CH<sub>2</sub>Cl[CH<sub>2</sub>]<sub>n</sub>C<sub>6</sub>H<sub>4</sub>N<sub>2</sub> and arylalkylamines or arylalkyl chlorides of the general formula aryl[CH<sub>2</sub>]<sub>n</sub>Cl and aminoalkylglyoxalines or the salts of these compds. are allowed to react with each other. By the action of 4-methyl-5-chloromethylglyoxaline hydrochloride on β-phenylethylamine, the secondary 5-phenylethylaminomethyl-4-methylglyoxaline and tertiary β-phenylethylaminodi(4-methyl-3-methylglyoxaline) are obtained which are sepd. by fractional crystn. of the picrates from acetone. The picrate of the secondary base, CH<sub>2</sub>Ph.CH<sub>2</sub>.NH.C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>.2C<sub>6</sub>H<sub>5</sub>O-N<sub>3</sub>, m. 208°, forms needles from hot glacial AcOH or thick plates from acetone; the hydrochloride crystallizes in plates, m. 249°, the chloraurate, m. 212°, forms yellow plates. The picrate of the tertiary base, CH<sub>2</sub>Ph.CH<sub>2</sub>.N(CH<sub>2</sub>.C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>Me)<sub>2</sub>.3C<sub>6</sub>H<sub>5</sub>O<sub>2</sub>N<sub>3</sub>, m. 174°, forms spangles from hot glacial AcOH contg. picric acid. By heating β-4-aminoethylglyoxaline with β-*p*-hydroxyphenylethyl chloride for 12 hrs. in dry MeOH under pressure at 100°, 4(5)-*p*-hydroxyphenylethylaminoethylglyoxaline, OH.C<sub>6</sub>H<sub>4</sub>[CH<sub>2</sub>]<sub>n</sub>.NH.[CH<sub>2</sub>]<sub>m</sub>.C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>, m. 156°, is obtained. The picrate m. 201°, and forms orange-red prisms and needles. The dihydrochloride, m. 199°, forms spikes from boiling alc. Which group is in the 4-, which in the 5-position in all these compds. is uncertain. J. C. S.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

## A—GENERAL

FRANK P. UNDERHILL

**Project of reform of nomenclature of biological chemistry.** G. BERTRAND. *Bull. soc. chim. biol.* 5, 95-109(1923). A. T. CAMERON

**Pasteur and biological chemistry.** E. DERRIEN. *Bull. soc. chim. biol.* 5, 155-76(1923).—A review. A. T. CAMERON

**Some physical chemical properties of laminarin.** MISS Z. GRUZEWSKA. *Bull. soc. chim. biol.* 5, 216-26(1923).—Laminarin is an unstable colloid, slowly undergoing a const. transformation. It is a typical sol composed of granules of different sizes, only the smaller showing Brownian movement. Its aq. soln. spontaneously decomposes, apparently through polymerization or condensation, for which O appears indispensable. It can pass through a collodion membrane. A 2% soln. in 5% NaOH on addn. of EtOH and Et<sub>2</sub>O in correct amt. yields on standing large rectangular plates which transform to networks of long needles. A. T. CAMERON

**Hemocyanin.** G. QUAGLIARIELLO. *Naturwissenschaften* 11, 261-8(1923).—A chem. and biol. review. C. C. DAVIS

**Enzymic regulation of the movement of the stoma.** FRIEDL WEBER. *Naturwissenschaften* 11, 309-16(1923).—A review with a bibliography. C. C. DAVIS

**Biochemical problems and processes.** L. ROSENTHALER. *Ber. pharm. Ges.* 33, 14-9(1923).—An address. W. O. E.

**The significance of the antagonism between potassium and calcium for physiology and pathology.** S. G. ZONDEK. *Klin. Wochschr.* 2, 382-5(1923).—A review including a discussion of the most recent literature on this subject with a good bibliography. MILTON HANKE

**Seasonal variations in the dissolved oxygen content of the water of the Thames estuary.** WM. BUTLER AND J. H. COSTE. *Biochem. J.* 17, 49-58(1923).—Water is apparently appreciably supersatd. with O even though in free contact with air. Marked alk. and supersatn. go hand in hand. Still weather tends to preserve supersatn.; when the water is agitated by wind supersatn. in the estuary disappears rapidly. "The O of supersatn. is but a proportion, and probably a small one, of the vol. set free by marine photosynthesis. It has always been realized that the sea acts as a great stabilizer of the CO<sub>2</sub> content of the air by reason of the bicarbonate-carbonate equil. It appears that it is equally efficacious in the positive work of keeping up by continual contributions a steady proportion of O in the air." B. HARROW

**Effect of carbon dioxide and acetic acid on the osmotic pressure of hemoglobin.** H. C. WILSON. *Biochem. J.* 17, 59-71(1923).—Hemoglobin was prepared according to Dudley and Evans (*C. A.* 15, 3856). The osmometer used was a Bayliss modification (*C. A.* 4, 405). The osmotic pressure of a soln. of purified hemoglobin is 3 or 4 times as great when dialized against AcOH or water satd. with CO<sub>2</sub> (both about  $p_H$  4), as against water alone. This is probably due to the formation of some sort of an ionizing salt of hemoglobin—either one which ionizes into several protein ions, or into protein and acetate or protein and bicarbonate ions. B. H.

**Note on hydrolysis of pectin.** FRANK TUTIN. *Biochem. J.* 17, 83(1923); cf. *C. A.* 16, 65.—Argument in favor of the view, previously expressed, that pectin is probably the dimethylisopropenyl ester of pectic acid. BENJAMIN HARROW

**Urease. I. The chemical changes involved in zymolysis of urea.** W. R. FEARON. *Biochem. J.* 17, 84-93(1923).—Evidence is brought forward to support Werner's hypothesis (*C. A.* 12, 680) that the hydrolysis of urea proceeds in two stages: (a)  $\text{CON}_2\text{H}_4 \rightarrow \text{NH}_3 + \text{HNCO}$  and (b)  $\text{HNCO} + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2$ . By the action of urease on urea, F. has been able to isolate cyanic acid as the silver salt. B. H.

**Reduction of methylene blue by tissue extracts.** G. M. WISHART. *Biochem. J.* 17, 103-14(1923).—Many tissues possess the property of reducing methylene blue. Prolonged washing of tissue removes this property, but Thunberg (*C. A.* 17, 457) has shown that when succinic acid is added to such a washed tissue, its power of reducing methylene blue is restored. The "succinodihydrogenase" removes hydrogen from the "donator," succinic acid, and transfers it to the "acceptor" (methylene blue in this case). W. finds that the reduction of methylene blue by muscle alone is a process which differs from the reduction which occurs in the presence of a "donator." The graphs are of dif-

ferent form. The graphs, whether for donator reduction or spontaneous reduction, do not resemble the graphs of ordinary enzyme reactions.

**Adsorption and hemoglobin.** W. M. BAYLISS. *Nature* 111, 666-7(1923).—A reply to Adam (*C. A.* 17, 2120). "Nearly all the workers on the problem direct their attention only to the investigation and interpretation of these phenomena from the point of view of mass action in a homogeneous system. While this may ultimately turn out to be the correct view, it must not be overlooked that hemoglobin under most conditions exists in the form of colloidal aggregates. Thus surface phenomena may intervene and should receive due consideration."

**The action of metallic copper on blood catalase.** M. HÄNDL AND E. SEGALL. *Z. Hyg.* 97, 1-11(1922).—Blood catalase is injured by metallic Cu, while the spontaneous decompn. of  $H_2O_2$  is not influenced. The injury to blood catalase by Cu is stronger in the light than in the dark and stronger in NaCl soln. than in  $H_2O$ .  $H_2O$  and glass vessels which have been in contact with Cu act as Cu alone. The action of Cu on catalase has the characteristics of the so-called oligodynamic action. The time course of decompn. of  $H_2O_2$  by catalase in the presence of Cu follows the law of monomolecular reactions.

**Pancreatic amylase and the chlorine ion.** H. BIERRY. *Compt. rend. soc. biol.* 87, 1111(1922).—Pancreatic and intestinal amylases freed of Cl by dialysis are inactive with both starch and glycogen; the presence of Br or Cl is essential for their activity. Sucrase of the intestine and maltase of the pancreas also lose their activity by dialysis but regain this partly on the addn. of Cl.

**Effect of different ions on pancreatic amylase.** H. DA FONSECA. *Compt. rend. soc. biol.* 88, 313-5(1923).—A general discussion of the influence of anions and cations.

**Effect of methanol on the coagulation of blood in vitro.** A. BERGMAN. *Compt. rend. soc. biol.* 88, 382(1923).—MeOH coagulates oxalated horse plasma. S. M.

**The quantitative idea in microbiology.** PH. LASSEUR. *Bull. sci. pharmacol.* 30, 219-23(1923).—An address.

**Selective ionic permeability of the cellular elements.** W. MESTREZAT, PIERRE GIRARD AND V. MORAX. *Compt. rend.* 174, 1727-9(1922).—In expts. upon the corneal membrane of rabbits, the dissociations observed in the passage of ions of a mol. in traversing a cellular or even endothelial barrier show that the permeability of the cells to the electrolytes is an ionic permeability which is elective. This is doubly proved in the corneal filtration and resorption at the level of the vessels. The ionic groupings, which will be found on the other side of a septum electively permeable to the ions are different from those of the initial medium. Cf. *C. A.* 17, 777.

**Physical scheme of the selective permeability of living cells to different ions.** PIERRE GIRARD, W. MESTREZAT AND LI-SHOW-HOUA. *Compt. rend.* 175, 133-5(1922); cf. preceding abstr. and *C. A.* 17, 777.—Among the factors which influence the selective permeability of the living cell wall is the condensation of ions of opposite signs in the thin layers of liquid adherent to the cell walls. The displacement toward a pole of the autonomous cells in a conducting medium subjected to the action of an electric field of force suggests the existence of such electrified layers. It may readily be shown that the condensation of charges of opposite signs occurs on the faces of an inert septum segg. two conducting mediums, of which one at least has a  $p_H$  different from neutrality. The septum is polarized without the intervention of electricity exterior to the system (cf. *C. A.* 4, 2513, 2897, 3086). Permeability expts. with  $BaCl_2$ ,  $BaI_2$  or  $MgCl_2$  on one side of a septum made of gold beaters skin and  $HNO_3$  on the other side, also  $Ba(NO_3)_2$  against  $CCl_3COOH$  showed that the ratio of the number of Ba or Mg cations diffused to that of the anions diffused is always much less than that of the chem. equivalence between cation and anion. The same is shown, but the difference is less marked, with univalent ions such as  $NH_4$  in  $NH_4Cl$ . Since the anions of the salt as well as those of the acid diffuse in large excess as compared with the cations, it is the H ions which restore the equil. charges in the diffusing medium. Addition of a salt of Ba or Mg to the soln. of a concd. acid strongly increases the diffusion of the H ions toward the water across the septum. Thus the polarized septum acts as a selective modifier of the mobility of the cations, favoring the passage of  $H^+$  and opposing the passage of Ba, Mg, etc. The concns., valencies and mobilities of the anions of the salts are practically the same as those of the anions of the corresponding acids. Differences in the permeability of the anions appear to be morphological and dependent on the complexity of the group. This is seen on comparing the permeability of  $NO_3$ , Cl or I with  $CCl_3COO$ . *In vivo* several additional factors must be considered.

**Reversibility of the fermentive action of  $\alpha$ -D-mannoside.** H. HERISSY. *Compt.*

*rend.* 176, 779-82(1923); cf. C. A. 15, 1733, 3120; 16, 1257, 2336.—In utilizing the  $\alpha$ -*d*-mannoside enzyme contained in germinating lucerne, one may according to the medium chosen obtain either the decompn. or synthesis of  $\alpha$ -methyl-*d*-mannoside. Thus in a mixt. (I) of  $\alpha$ -methyl-*d*-mannoside 1.0007 g., MeOH (99.5%) 10 g., dry powder of germinating lucerne 4, toluene 1 cc. and H<sub>2</sub>O up to 100 cc.,  $\alpha$ -methyl-*d*-mannoside is hydrolyzed. With (II) in which *d*-mannose 0.928 g. (corresponding to 1.0007  $\alpha$ -methyl-*d*-mannoside) is substituted for the  $\alpha$ -methyl-*d*-mannoside of I the  $\alpha$ -methyl-*d*-mannoside is synthesized. A suitable control was carried on the reagents. These mixts. were allowed to stand at lab. temps. with occasional shaking for about 6 months until polariscopic observation showed no further change. The products were then calcd. from the polariscopic readings and the reducing sugar values. L. W. RIGGS

**Hydrolysis of maltose by extract of malt.** L. MAQUENNE. *Compt. rend.* 176, 804-6(1923).—Expts. were made with an ext. of malt contg. 100 g. of malt powder to 1 liter of cold water with toluene as an antiseptic. One-half of this malt ext. was allowed to act on a soln. of maltose contg. 0.478 g. in 100 cc., and the other half after diln. with 10 vols. of water on a soln. contg. 0.438 g. of maltose per 100 cc. Each of the 2 series of liquids was divided into 3 portions, always in the presence of toluene, and maintained at 15, 50 and 60°, resp., for 6 days. The amt. of reduction was detd. each day in the liquids of both series and in the malt alone. These tests gave concordant results although varying ten fold in the concn. of the malt ext. It appears that the ext. of malt is the source of a continuous transformation with a gradually increasing reducing power up to a limit which varies with the temp. L. W. RIGGS

**The law of living reaction (vivreaction) in biology and in pathology.** JULES AMAR. *Compt. rend.* 176, 921-4(1923).—By the phrase, law of living reaction, is understood all acts pathological or physico-chemical, which tend to diminish the phenomena of oxidation organically provoked, by a mechanism of defense, with a relative increase of the pulmonary ventilation. It is a nervous mechanism for the defense of cellular combustion, remarkable especially in animals with a const. temp. This subject is discussed by the aid of many familiar examples. **The law of living reaction in pathology.** *Ibid.* 1021-4.—The law is shown to apply in fever and in pulmonary tuberculosis. The integrity of the nervous centers is the best arm for the normal defense of the life. L. W. RIGGS

**Imitation of plasmodia and chromatic structures with sodium silicate blackened with ivory black, and with drops of alcohol in diffusion.** A.-L. HERRERA. *Compt. rend.* 176, 1011-2(1923); cf. C. A. 14, 416. L. W. RIGGS

**Minimum concentration of luciferin to give a visible luminescence.** E. N. HARVEY. *Science* 57, 501-3(1923); cf. C. A. 10, 74, 2483, 3077; 11, 1212, 2906, 3059.—Luciferin is the substance of luminous animals which produces light when oxidized. An enzyme, luciferase, likewise found in luminous animals, must be present for light production. In 1916, H. calcd. that one part of luciferin from *Cypridina* in 1,700,000,000 parts of sea water when mixed with luciferase gave light visible to the unaided eye. Recent expts. prove that light from a weaker soln. may be seen, the figures being 1 part luciferin in 4 to 40 billion parts of sea water. Also 1 part of pure luciferase in 800 million to 8 billion parts of sea water will oxidize a stock luciferin soln. with visible luminescence. Exptl. details are given. A glass cylinder which had contained a stock luciferin soln. was washed with 15 changes of warm water; when it was filled with sea water and luciferase added it showed light. Sea water in other cylinders which had not held a luciferin soln. gave no light. L. W. RIGGS

**Physical chemistry of phagocytosis.** TOKUJIRO KANAI. *Arch. ges. Physiol.* (Pflüger's) 198, 401-14(1923).—The phagocytosis of charcoal by leucocytes is initiated by an adhering of the carbon particles to the surface of the cell. This adhesion is the result, if it takes place in protein-contg. solns., of the operation of the same principles which govern the agglutination of erythrocytes in protein solns. Plasma favors phagocytosis, or at least, the drawing together of leucocyte and charcoal, more than does serum; fibrinogen more than pseudoglobulin; and pseudoglobulin more than albumin. The attraction between leucocyte and charcoal is weaker if the protein soln. in which they are suspended has been previously heated to 42°, although it is not altered if the soln. has been shaken during the heating. The influence of various solns. upon the clumping of leucocytes and charcoal particles parallels the effects of these solns. upon the agglutination and sedimentation of leucocytes and red cells. While saline solns. do not favor the sedimentation of erythrocytes they do markedly increase the agglutination and sedimentation of leucocytes, and at the same time stimulate the attraction between the white cell and the particles of charcoal. This difference between red and white cells is apparently referable to the fact that in saline the leucocytes are but weakly

charged, while the red cells bear a strong negative charge. In low concns.  $\text{CaCl}_2$  stimulates phagocytosis; in high concns. it is inhibitory. This is also true for the agglutination and sedimentation of both red and white cells. Suspensions of inorg. matter in protein solns. behave in much the same manner as do blood cells. The different effects of the various serum proteins are associated with their varied capacities for adsorption. Pseudoglobulin adsorbs more strongly than does albumin, and the capacity for adsorption by pseudoglobulin is greatly increased by small amts. of  $\text{CaCl}_2$ . G. H. S.

**Autoxidations.** III. E. ABDERHALDEN AND E. WERTHEIMER. *Arch. ges. Physiol. (Pflüger's)* 198, 415-20(1923); cf. C. A. 17, 2121.—The conversion of aldehydes into acids and alcs. (Cannizzaro's reaction) by tissues (liver, muscle) is modified by the addition of cystine or cysteine. With the first more acid is produced; with the second, more alc. The change of  $\beta$ -hydroxybutyric acid to acetoacetic acid is also modified. Apparently the system cystine  $\rightleftharpoons$  cysteine is a mechanism which enables the cells to bring about the transformation of aldehydes into acids and alcs., now favoring the formation of the one, at another time favoring the production of the other. Possibly oxido-reduction processes in general may be influenced at one time in favor of oxidation, at another time in favor of reduction. S acts like cystine, although less strongly. Cystine added to a soln. of dextrose diminishes the reduction activity. G. H. S.

**Swelling and shrinking phenomena in chondriosomes.** N. ANITSCHKOW. *Arch. mikroskop. Anat.* 97, 1-14(1923).—The external form of the chondriosome is directly dependent upon the osmotic conditions of the surrounding medium. With changes in the  $\text{NaCl}$  concn. of the surrounding fluid all possible forms of chondriosome can be observed in a single cell. The expts. were performed upon the liver cells of the axolotl, the liver cells of frogs and rabbits, and the heart muscle fibers and kidney cells of frogs. The saline solns. varied in concn. from 0.1 to 1%. G. H. S.

**Atom and cell.** F. S. LONDON. *Arch. mikroskop. Anat.* 97, 43-53(1923).—The similarities between the atom and the cell, the units of living matter, are discussed. The atom contains a nucleus with an external layer of material, and so does the cell. The nucleus of the atom contains particles bearing a positive charge; so also does the cell nucleus contain positively charged particles, as is shown by their reactions with negatively charged dyestuffs. In the outer layer of the atom are particles with a negative charge; the cytoplasm of cells likewise contains particles bearing a negative charge, since they combine with acid dyes. The positive charge of the nucleus of the atom is revealed by the presence of He and H ions; that of the cell nucleus through the presence of H ions which become dissociated from the nucleic acid of the chromatin. The negative charge of the body of the atom is shown by the negative electrons; that of the cell from those arising from the radioactive K. The type of an atom and its position in the chem. system are detd. by the no. of positively charged particles of the nucleus, e. g., Be 4, Ti 24, Ce 72. The type of a cell and its position in the zool. system are detd., as it were, by the no. of positively charged chromatin particles, the chromosomes, e. g., in ascaris 4, in man 24, in the calf 72. The individuality of the atom is detd. by the complex of the positively charged particles; loss of any portion alters the nature of the atom, as in Ra, Th, and Ac. Similarly, in the cell, the loss of positively charged chromosomes changes the nature of the cell, as from the egg cell to the body tissue cell. The analogy is carried further through many points of similarity. G. H. S.

**Structure of pearls, with particular reference to their crystalloid elements.** W. J. SCHMIDT. *Arch. mikroskop. Anat.* 97, 251-82(1923).—Normal pearls are formed from the materials of the shells of the shell-fish, and their structure is detd. by the form in which the Ca crystallizes. These forms are described. G. H. S.

**Keratin.** II. A. HEIDUSCHKA AND E. KOMM. *Z. physiol. Chem.* 124, 37-64(1922); cf. C. A. 17, 114.—A study of the fractions into which the decompn. products of keratin may be sep'd. by pptn. with  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{ZnSO}_4$  in neutral and acid soln. and the concn. limits for each fraction. Four fractions were obtained with each salt. R. L. STEHLE

**Invertase.** IV. R. WILLSTÄTTER AND W. WASSERMANN. *Z. physiol. Chem.* 123, 181-96(1922); cf. C. A. 17, 1972.—Highly concd. solns. of invertase were prepd. with much more facility than formerly, by conducting the adsorption with kaolin or  $\text{Al}(\text{OH})_3$  in highly dil'd. (20-fold) autolyzates, utilizing in addition dialyzing and evapn. procedures. A quantity of kaolin insufficient to adsorb all the invertase was first employed and the filtrate then treated with a second quantity of kaolin. By this preliminary kaolin treatment substances which usually accompany the invertase are eliminated. One invertase prepn. (with  $\text{Al}(\text{OH})_3$  as absorbent) contained no gum and gave only a

faint Millon reaction. Another prepn. (with kaolin) was also free from gum, and gave no Millon test but reacted positively with ninhydrin. R. L. STEHLE

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## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

**The chromophyl reaction in histology and its signification.** J. VERNE. *Bull. soc. chim. biol.* 5, 227-35(1923).—Microchem. study shows that the chromophyl reaction is not specific, but is characteristic of compds. with a benzene ring, and either 2 OH groups or one OH and one amine group in the *o*- or *p*-position. It is not given by amino acids. The reaction with the posterior salivary glands of the octopus is due to tyramine. The staining reactions are less intense with tyramine than with adrenaline. The reaction is commoner with vegetable than with animal tissues because of the presence of phenol compds. A. T. CAMERON

**Estimation of sugar in the blood.** E. G. B. CALVERT. *Biochem. J.* 17, 117-29 (1923).—The principle employed is based on the methods employed by Folin and Wu (*C. A.* 13, 2541; 14, 2353) and Wallis and Gallagher (*C. A.* 16, 2907). The details are much too involved to be abstracted. The main features of the method are (a) collection and weighing of blood in a special capsule, (b) a fixed color standard in glass, (c) use of a curve of correction for copper reduction. BENJAMIN HARROW

**Exposure to light as a source of error in estimating uric acid by the Folin and Wu method.** HOBART ROGERS. *J. Biol. Chem.* 55, 325-31(1923).—The estn. of uric acid in blood by the Folin-Wu method is likely to give low results when conducted at ordinary speed in a well lighted lab. Centrifuge tubes with their contained Ag ppts. should be kept constantly in trunnion-cups shielded with tin foil until the liberated uric acid has been decanted. With slight exposures the loss is nearly proportional to the exposure but proceeds more slowly as the amt. of uric acid in the soln. is reduced. The loss is increased by increasing the H-ion concn. A. P. LOTHROP

**A new method for the separate extraction of vacuole and protoplasmic material from leaf cells.** A. C. CHIBNALL. *J. Biol. Chem.* 55, 333-42(1923).—If leaf cells are first plasmolyzed by means of org. agents such as  $\text{Et}_2\text{O}$ ,  $\text{BuOH}$ , etc., the major portion of the vacuole content can be pressed out in a Büchner press and the remainder can easily be washed out by repeatedly allowing the pressed residues to imbibe 0.002 N HCl and subsequently pressing. This operation does not rupture the leaf cells and the protoplasm, from which some of the  $\text{H}_2\text{O}$ -sol. constituents may have been washed out, is retained within them. The protoplasmic material remaining in the residue can be extd. by grinding with  $\text{H}_2\text{O}$  into which it passes in colloidal soln. and can subsequently be flocculated by acid. It is composed of substances sol. in alc. and  $\text{Et}_2\text{O}$  together with a complex the greater part of which is protein. Part of the protoplasmic protein passes into soln. if  $\text{H}_2\text{O}$  instead of HCl is used for washing the pressed residue. The ppt. obtained by the addn. of acid contained 14.9% of N and is sol. in small excess of either acid or alkali. With spinach leaves a 1 min. immersion in  $\text{Et}_2\text{O}$  brings about an extreme degree of flaccidity. A. P. LOTHROP

**The refractometric determination of serum proteins.** B. S. NEUHAUSEN AND D. M. ROACH. *J. Biol. Chem.* 55, 353-6(1923).—More accurate results are obtained on the av. by deducting from the *n* of human serum that for distd.  $\text{H}_2\text{O}$  at the temp. plus 0.0022 for non-protein constituents and dividing by 0.00194 than can be obtained by the procedure of Reiss who uses the figures 0.00277 and 0.00172. A. P. L.

**Colorimetric determination of iron and hemoglobin in blood.** SAN YIN WONG. *J. Biol. Chem.* 55, 421-5(1923).—Measure 1 cc. of blood into a test-tube contg. exactly 4 cc. of  $\text{H}_2\text{O}$ . After shaking rinse the pipet 3-4 times. With the same Ostwald pipet transfer 1 cc. of the dild. blood to a Pyrex test-tube,  $25 \times 200$  mm., graduated at 25 cc. Add 1 cc. of Fe-free concd.  $\text{H}_2\text{SO}_4$  and a glass bead. Clamp the tube in a buret clamp.



Boil vigorously over a micro-burner until the tube is filled with white fumes. Cover with a watch glass and continue to boil vigorously for  $3\frac{1}{2}$  min. Cool for 20 sec. Adjust the test-tube to an angle of about  $40^\circ$  and add, drop by drop from a 1 cc. pipet, 1 cc. of 10%  $\text{NaClO}_3$ . Let the drops fall on to about the middle of the test-tube and exercise care as the action is vigorous especially on adding the first few drops. Readjust the tube to the vertical position and boil for 3 min. Again turn the tube to  $40^\circ$  and add 0.3 cc. of  $\text{NaClO}_3$ . Boil again for 2 min., covering the tube when it is filled with white fumes. Cool for 1 min. Add 5 cc. of  $\text{H}_2\text{O}$ , avoiding spattering by running the  $\text{H}_2\text{O}$  down the side of the tube in an inclined position. Add more  $\text{H}_2\text{O}$  to make about 16 cc. Cool to room temp. under the tap. In another Pyrex tube place 1 cc. of standard Fe soln. contg. 0.1 mg. of Fe per cc. Add 1 cc. of concd.  $\text{H}_2\text{SO}_4$  and dil. with  $\text{H}_2\text{O}$  to 16 cc. Cool to room temp. Add to both tubes 5 cc. of 3 N KSCN or  $\text{NH}_4\text{SCN}$  and dil. to 25 cc. Mix and compare in a colorimeter. *Calc.*—reading of standard/reading of unknown  $\times 50 =$  mg. of Fe per 100 cc. of blood. To obtain the % of hemoglobin, divide this no. by 3.35 since hemoglobin contains 0.335% of Fe. *Standard Fe soln.*—Dissolve 0.7 g. of cryst.  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in 50 cc. of  $\text{H}_2\text{O}$ . Add 20 cc. of 10% Fe-free  $\text{H}_2\text{SO}_4$ , warm and then add 0.1 N  $\text{KMnO}_4$  to oxidize the ferrous salt completely. Dil to 1 l. For stronger or weaker standards dil. the regular standard 10 times and, as occasion demands, pipet out the no. of cc. necessary to give 0.06 to 0.15 mg. of Fe.

A. P. LOTHROP

The use of persulfate in the estimation of nitrogen by the Arnold-Gunning modification of Kjeldahl's method. SAN YIN WONG. *J. Biol. Chem.* **55**, 427-30(1923).—Transfer 5 cc. of urine, dild. (1 : 5) blood, or milk or 0.5 g. of dry protein to an 800 cc. Kjeldahl flask. Add 2 cc. of 5%  $\text{CuSO}_4$ , 5 g. of pure  $\text{K}_2\text{SO}_4$ , 20 cc. of N-free  $\text{H}_2\text{SO}_4$ , and a few clean quartz pebbles. Heat gently until vigorous frothing ceases and then strongly until the acid mixt. becomes amber colored (20-30 min., 10 min. with urine). Allow to cool for 10 min. While holding the neck of the flask with a towel, allow 3 cc. of distd.  $\text{H}_2\text{O}$  to flow down the side of the flask at the same time rotating gently. Set the flask upright at once and add 10 g. of  $\text{K}_2\text{S}_2\text{O}_8$  (3 g. with urine) taking care that as little of the powder as possible adheres to the neck of the flask. Rotate to mix thoroughly and reheat at once until the mixt. becomes green (15 min.). Complete the detn. in the usual manner. With the digestive mixt. cooled for 10 min. and with the introduction of the  $\text{H}_2\text{O}$ , the oxidation by the  $\text{K}_2\text{S}_2\text{O}_8$  takes place at a comparatively low temp., the danger of explosion is avoided, no loss of N occurs and the time of digestion required is about  $\frac{2}{3}$  of that in the old method. The use of persulfate in the estimation of nitrogen by Folin's direct Nesslerization method. *Ibid* 431-5.—*Urine*—Dil. the urine so that 1 cc. contains 0.2-0.3 mg. of N (ordinarily 2 cc. dild. to 100). Transfer 1 cc. of the dild. urine with an Ostwald pipet to a large Pyrex test-tube graduated at 35 and at 50 cc. Add 1 cc. of 1 : 1  $\text{H}_2\text{SO}_4$  and a quartz pebble. Boil vigorously with const. shaking over a microburner until most of the  $\text{H}_2\text{O}$  is expelled. Clamp the test-tube in a buret clamp and boil until white fumes begin to fill the tube. Cover with a watch glass as soon as the tube is nearly full of fumes and reduce the flame so that the mixt. boils gently. Continue the gentle boiling for 2 min. Allow to cool for 1 min. Add 2 drops of satd.  $\text{K}_2\text{S}_2\text{O}_8$  soln. (7 g. per 100 cc. of distd.  $\text{H}_2\text{O}$ ) with a fine pipet or dropper. Boil until the mixt. becomes colorless. Stop the boiling about 15 sec. after the reappearance of white fumes, the tube being covered with a watch glass during this period. Cool for 70-90 sec. Add 20-25 cc. of  $\text{H}_2\text{O}$  and cool to room temp. under the tap. Dil. to the 35 cc. mark. To 2 cc. of a standard  $(\text{NH}_4)_2\text{SO}_4$  soln. containing 0.1 mg. of N per cc. in another Pyrex tube add 1 cc. of 1 : 1  $\text{H}_2\text{SO}_4$  and dil. to the 35 cc. mark. To both tubes add 15 cc. of Nessler's soln. (prepd. according to Folin, *C. A.* **13**, 2542), letting the Nessler's soln. fall directly into the acid soln. so that it is thoroughly mixed thereby. Insert a clean rubber stopper, mix and compare in a colorimeter. *Blood*—Dil. blood 150 times and use 1 cc. for the detn. Heat 3 min. after the tube becomes filled with fumes and use 0.5 cc. of satd.  $\text{K}_2\text{S}_2\text{O}_8$  soln. *Milk*—Dil. milk 20 times and use 1 cc. in the detn. Heat 4 min. after the tube becomes filled with fumes and use 1 cc. of the satd.  $\text{K}_2\text{S}_2\text{O}_8$  soln. About 2 min. heating is usually required after the reappearance of the white fumes before the digestive mixt. becomes colorless. A. P. LOTHROP

The occurrence of aldol in diabetic urine. R. FRICKE. *Z. physiol. Chem.* **124**, 1-7(1922); cf. *C. A.* **16**, 2736.—The method previously employed was not quant. Improvements are described.

R. L. STENLE

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### C—BACTERIOLOGY

A. E. BALLS

**Oxidation of zinc sulfide by microorganisms.** W. RUDOLFS AND ANDRÉ HELBRONNER. *Soil Science* 14, 459-64(1922).—A mixed culture of S-oxidizing organisms was able to transform  $ZnS$  to  $ZnSO_4$ . The transformation was rapid at  $pH$  values as low as 5.5. The soluble Zn was not toxic to the organisms. Low-grade  $ZnCO_3$  and Zn silicate ores were rendered sol. when composted with inoculated S. The possibility of a biological method for the economic utilization of low-grade ores is pointed out.

R. BRADFIELD

**The synthetic action of bacteria in the paunch of the cow.** B. SJOLLEMA AND J. E. VAN DER ZANDE. *Proc. Acad. Sci. Amsterdam* 25, 482-6(1923).—A study of the ability of bacteria from the paunch of the cow to synthesize tryptophan and tyrosine from urea and from  $NH_3$  plus asparagine N. *In vitro* the results were positive. "It is uncertain whether this synthesis is equally intense in the paunch." HARRY J. DEUEL, JR.

**The production of tyrosine by a putrefactive anaerobe.** I. C. HALL AND FLORENCE FINNERUD. *Proc. Soc. Exptl. Biol. Med.* 19, 48-50(1921); *Botan. Abstracts* 11, 457.—A method is described for extg. crystals of tyrosine from a pure culture of an unknown putrefactive anaerobe. H. C.

**Phagocytosis of the bacteriophage.** R. BRUYNOGHE AND J. MAISIN. *Compt. rend. soc. belge biol.* 1922, 30-1; *Physiol. Abstracts* 7, 137(1922).—The bacteriophage, like bacteria, undergoes phagocytosis, hence may disappear from the focus of suppuration. Therefore, it is frequently necessary to repeat the inoculation with bacteriophage in order to influence definitely the course of certain staphylococcal lesions.

JOSEPH S. HEPBURN

**Preliminary observations on the action of Bryonia.** A. G. NAST. *J. Am. Inst. Homeopathy* 15, 885-91(1923).—In dilns. of 1:9, *Bryonia* inhibits the growth of *B. diphtheriae* and *Staphylococcus albus*, and retards the growth of *Staphylococcus aureus*, *B. dysenteriae*, *B. typhosus*, and the Friedländer bacillus for 24 to 96 hrs. Higher dilns. apparently have no action on these organisms. The viability of organisms is not injured by repeated subcultures through media contg. *Bryonia* in the diln. 1:9.

JOSEPH S. HEPBURN

**The biological action of nitral and its significance for the hygiene of food.** HEINRICH BART. *Arch. Hyg.* 91, 1-40(1922).— $N_2O$  when mixed with  $H_2O$  vapor is called nitral. When dry  $N_2O$  is applied under pressure to bacteria it has no bactericidal action. Nitral, however, under the same conditions does have marked bactericidal action. Milk and meat when kept under pressure in an autoclave filled with nitral were made almost sterile after a period from several days to several weeks. The taste and nutritional properties of these foods underwent no change. JULIAN H. LEWIS

**Disinfectant action of tobacco smoke.** GEORGE WOLFF. *Arch. Hyg.* 91, 332-8(1922).—Tobacco smoke is proved to have a marked disinfectant action against *B. influenzae* and *B. prodigiosus*. The disinfectant substance in tobacco smoke can be washed out by  $H_2O$  but is not lost by filtration through cotton. JULIAN H. LEWIS

**Reduction experiments with bacteria.** LUDWIG GOZONY AND EUGEN KRAMAR. *Centr. Bakt. Parasitenk. I Abt.* 89, 193-209(1922).—A 24-hr. agar culture of bacteria will reduce better than an older one, but the difference is only apparent and is due to the fact that a 24-hr. culture contains more bacteria than an older one. Reduction takes place best in a slightly alk. medium and is better in neutral than acid reaction. Various salts vary in their influence on the reduction of methylene blue among the different bacteria. A mixt. of  $CaCl_2$  and  $NaCl$  solns., which by themselves are either indifferent or inhibitive, markedly stimulates methylene blue reduction. Reduction takes place best at the temp. at which the bacteria grow. Proteins and protein derivs. generally promote reduction and vary in the same way as they support growth. There seems to be a parallelism between virulence and reducing action of bacteria. Reduction of methylene blue by bacteria is chiefly the result of vital processes occurring within the cell, although there is a slight action by extracellular substances, probably fermentative in action. JULIAN H. LEWIS

**The bactericidal and inhibitive action of yatren.** ALFRED BREITENSTEIN. *Centr. Bakt. Parasitenk. I Abt.* 89, 294-312(1923).—Yatren is an org. I prepn. which contains yatren acid and has been much used in the treatment of infectious diseases. In this paper the bactericidal action against various pathogenic organisms is tested.

Yatren does not possess a general strong bactericidal action. It acts most strongly on streptococci, *B. anthracis* and *B. chauvei*. Its *in vitro* action is out of proportion to its reported *in vivo* action and is thought to be due to some nonsp. action of yatren on the tissues.

JULIAN H. LEWIS

**The toxic action of nitrates on lower organisms.** HILDEGUND BÖTTGER. *Centr. Bak. Parasitenk. II Abt.* 50, 220-61 (1921).—In certain concns. nitrate solns. are toxic. With increasing concns. the toxic action increases until the protoplasm is killed. The limits of the concns. at which nitrates act on organisms depend on the species studied. It also depends on the condition of life, *i. e.*, the nitrates are more toxic for yeasts in artificial media than plant "pressaft." The different functions of organisms are injured unequally. The toxicity has to do with the fact whether nitrates are concerned in the normal metabolism or not. When certain concns. of nitrate enhance the growth of organisms it is due to the nutritive action of the N. With alc.-forming yeasts, which do not attack nitrates no such stimulation is observed. Instances are given to show that the toxic action of nitrates may be due to osmotic pressure, the metallic ion or the  $\text{NO}_3$  ion.

JULIAN H. LEWIS

**The influence of hydrogen-ion concentration on bacterial types.** P. R. CANNON AND B. W. MCNEARE. *J. Infectious Diseases* 32, 175-80 (1923).—The actual acidity of the intestinal contents of the cecum and colon of white rats is an important factor in the simplification of the intestinal flora. With a high animal protein diet the reaction of the contents of both the cecum and colon is  $p_H$  7.0 to 7.1 whereas the addn. of lactose in proper proportions may lead to a  $p_H$  in the cecum of 4.6 with a  $p_H$  of 6.2 in the lower colon. Therefore detns. of the actual acidity of feces are of slight value in interpreting the reaction of the intestinal contents higher up. The simplification of the intestinal flora varies directly with the H-ion concn., a  $p_H$  of 7.0 being characteristic of a gas-producing proteolytic type, whereas an increasing acidity is characterized by a diminution of proteolytic types and their replacement by aciduric types mainly dominated by *B. acidophilus*.

JULIAN H. LEWIS

**Bacteriostatic action of dyes on *Streptococcus viridans* and pneumococcus.** J. F. NORTON AND G. E. DAVIS. *J. Infectious Diseases* 32, 220-2 (1923).—The organisms belonging to *Streptococcus viridans* and pneumococcus groups are inhibited by dyes to the same extent. It is therefore not feasible to use any dye for differential purposes. To have marked bacteriostatic action, a dye must contain 3 benzene and 2 or more amino groups in which the H atoms have been substituted by alkyl radicals. Acid dyes or salts of acid or basic dyes are practically inert.

JULIAN H. LEWIS

**Action of acridine dyes on infected wounds.** K. WEISS. *Z. Hyg.* 97, 56-76 (1922).—Mice with wounds infected with various strains of streptococci were saved by treating the wounds with rivanol and trypanflavin. Vucine was not nearly as active as the acridine dyes.

JULIAN H. LEWIS

**Chemotherapeutic biology of microorganisms.** J. MORGENROTH AND R. SCHNITZER. *Z. Hyg.* 97, 77-88 (1923).—Hemolytic streptococci when passed through mice produced green nonhemolytic colonies. The green-producing organisms were 4-8 times more resistant to rivanol than the hemolytic ones. With vucine in 2 cases there was no change; in 2 cases the green organisms were half as resistant and in 2 other cases they were 2-4 times more resistant.

JULIAN H. LEWIS

**Methemoglobin plates for the differentiation of streptococci.** ARTHUR SEITZ. *Z. Hyg. Infektionskrankh.* 96, 216-24 (1922).—Methemoglobin plates are prepd. by adding 5% of rabbit or sheep blood to agar at 72-4°. The plates are brown in color. Streptococcus and pneumococcus produce greenish yellow colonies with a wide diffusion band of discoloration while the hemolytic streptococci produce a yellowish "milk and coffee" color. A green iridescent band is characteristic of *Streptococcus viridans*.

JULIAN H. LEWIS

**In vitro action of acridine and other dyes on bacteria.** O. SCHIEMANN AND W. BAUMGARTEN. *Z. Hyg.* 97, 247-79 (1923).—This is a general discussion of acridine and other dyes. Such questions are considered as chem. constitution, selective action, active limit of diln., and effect of medium on bactericidal action.

J. H. L.

**The antagonistic action of gelatin and agar on the bacteriophage reaction.** R. DOERR AND W. BERGER. *Z. Hyg.* 97, 422-32 (1923).—Gelatin, agar and other colloids (gums, sol. starch) inhibit the bacteriophage reaction. Gelatin produces inhibition in the fluid state as well as in the solid state. The antagonistic action of gelatin increases with its concn. Between equal concns. of agar and gelatin there is no difference of action. The antibacteriophage action occurs at 15° as well as at 37°. When gelatin inhibits the bacteriolysis there is still some evidence of influence of the bacteriophage on the bacteria, such as agglutination, lysis production, production of organisms with

increased resistance to bacteriophage reaction. All phenomena which are present in a bouillon culture to which bacteriophage has been added are present in the gelatin culture, except bacteriolysis. These colloids probably act as protective colloids against injury to the cell membrane which is believed to occur in the action of the bacteriophage. Since in fluid gelatin bacteriolysis does not occur, but lysin production is just as marked as in bouillon cultures, it is improbable that lysin comes from disintegration of the bacteria.

JULIAN H. LEWIS

**The culture of *Bacillus pyocyaneus* on chemically definite media.** A. LIOT. *Ann. inst. Pasteur* 37, 234-74 (1923).—The presence of an  $\text{NH}_4$  salt is necessary to the formation of the pigment pyocyanin. The formation can occur in a medium in which  $\text{NH}_4$  is not originally present, if the modifications in the medium produced by growth favor the production of  $\text{NH}_4$ . In the presence of certain acids  $\text{NH}_4$  is not only necessary, but suffices, for the production of pigment. The monobasic fatty acids  $\text{AcOH}$ ,  $\text{PrOH}$ ,  $\text{BuOH}$ , valeric and caproic acids are favorable to the growth of the bacillus and the production of pigment. Formic acid is unfavorable. Isocaproic acid permits growth but not the formation of pyocyanin; in a mixt. of caproic and isocaproic acids the presence of the former can be detected by the development of pigment on inoculation with *B. pyocyaneus*. The unsatd. monobasic fatty acids are unfavorable to growth, with the exception of sorbic acid. The salts of the monobasic and dibasic aromatic acids are unfavorable to development. The salts of the dibasic acids of the succinic acids series, with the exception of oxalic acid, favor growth. Of the doubly unsatd. dibasic acids only the salts of the acids in the *trans* position permit the production of pigment, those in the *cis* position being inactive in this respect. Hydroxy and ketonic acids of the lactic and pyruvic acid type favor the formation of pyocyanin. The phenolic acids are unfavorable. The dibasic acids having alc. radicals are active only when some C atoms are not attached to hydroxy groups; e. g., tartaric acid does not support as good growth as citric acid. Optical isomerism does not seem to play a role comparable to the stereo-isomerism in the unsatd. dibasic series. Amines and acid amides are not favorable sources for growth. Urea may support growth in carbohydrate media, on conversion into  $\text{NH}_4\text{CO}_2$  and union with org. acids. Amino acids support growth, best in the presence of carbohydrates and under conditions favoring the liberation of  $\text{NH}_4$  by deamination. Mineral  $\text{NH}_4$  salts and carbohydrates and alcs. employed separately do not support growth. In conjunction they supported growth in the case of the alcs. glycerol and mannitol, and the hexoses dextrose and levulose in the presence of  $\text{CO}_2$  and  $\text{NO}_2$ . With other sources of C growth was poor and pigment did not develop. Pyocyanin is formed only under conditions where an org.  $\text{NH}_4$  salt occurs. Protein is a poor source of nutrition unless it contains sufficient free amino acids or  $\text{NH}_4$  salts to enable development to start.

E. R. LONG

**The increase in virulency of non-pathogenic microorganisms by chemical substances.** R. H. LEE and LLOYD ARNOLD. *J. Lab. Clin. Med.* 8, 462-4 (1923).—Addn. of lactic acid to culture media and its simultaneous injection with *B. subtilis* both failed to make this microorganism virulent for mice. Similar results were obtained with *B. proteus*. A slight apparent increased toxicity of *B. proteus* when simultaneously injected with lactic acid is explained by the chem. impairment of the defensive mechanism of the host, rather than by a change in the biological characteristics of the microorganism. The results of Much (*C. A.* 17, 136) are thus not confirmed. E. R. L.

**Behavior of avirulent bacteria in the animal body under the action of lactic acid.** JOSEF FUCHS. *Z. Immunitäts.* 36, 122-32 (1923).—Treatment of cultures of *B. mycoides*, *B. subtilis* and *B. mesentericus* with varying concns. of lactic acid did not render them virulent for mice, nor could pathogenicity be conferred on the hay bacillus by growth in bouillon contg. lactic acid. *B. proteus vulgaris* did not harm mice either when injected simultaneously with lactic acid or when the acid was injected 5 hrs. before the bacilli.

E. R. LONG

**The preservation of diagnostic fluids of typhoid and paratyphoid fever.** T. TOYAMA. *Intern. Med. News* No. 1021 (1923); *Japan Med. World* 3, 32 (1923).—T. tested comparatively, formalin, phenol, toluene, and chloroform emulsions of the bacilli, and found that chloroform answers the purpose best. This emulsion had the same degree of accuracy as the formalin emulsion, and kept for 6 mo. M. E. MAVER

**The changes in the biological nature of *Bacillus typhosus* by passing through the immune serum medium and immunized animal body.** S. YANAGISAWA. *Japan Med. World* 3, 19-26 (1923).—By cultivating the typhoid bacillus in the immune serum broth, a strain which has a weaker agglutinability, and is less liable to be absorbed, can be obtained. These changes are only transitory, and the original nature of the organisms can be restored by passing through the animal body twice, or by recultivating on common

agar. The changed bacilli have an unchanged antigenic property for agglutinin production, but a clearly lessened antigenic power for opsonin production. The treated bacilli combine less completely with the immune substances in the immune serum than do the normal strain. Their virulence is diminished. The typhoid bacillus that has been passed through the immunized animal body has an augmented and spontaneous agglutinability. This change is not reversible; the original nature cannot be restored by passing through the animal body or by growing on common media. These bacilli have a remarkably increased susceptibility to the sp. opsonin, and their virulence is increased.

M. B. MAVER

A new medium favorable for pigment production by staphylococcus, and also a contribution to the knowledge of pigment production. A. FUJITA AND S. YOSHIOKA. *Japan Med. World* 3, 47(1923).—Galactose, fructose, glucose, and lactose promote pigment production. The medium was ordinary agar with a known amt. of sugar added. Two vols. of this medium were added, when melted, to 1 vol. fresh milk after it had been sterilized by boiling and cooled. Pigment production is most marked at a  $p_H$  of 6.0 or slightly lower. Those organisms, which have yellow, orange, or rose pigments, and belong to the carotin group of Lehmann and Neumanna, produce much more pigment on this medium than do those organisms which produce pigments of the prodigiosin group, fluorescent pigments or brown pigments. Fats, especially palmitin, stearin and olein, promote pigment production. Lipoids have no such action. With some exceptions, the color formed is proportional to the fat- or sugar-splitting property of the organism. The split products, oleic acid, and glycerol, promote pigment production. Lower fatty acids and inorg. acids do not affect it.

M. E. MAVER

Excretion by microbes of phosphorus compounds. Effect of formalin during the first hours of contact. E. POZERSKI AND M. M. LÉVY. *Compt. rend. soc. biol.* 88, 259-60(1923); cf. C. A. 17, 1978.—The capacity for reproduction of a bacterial emulsion is soon destroyed by contact with formalin but the microbes continue to excrete phosphates for a time. This excretion stops after a while.

S. MORGULIS

Butylene glycol fermentation of glucose by certain bacteria of the *Bacillus proteus* group. M. LEMOIGNE. *Compt. rend. soc. biol.* 88, 467-8(1923); cf. C. A. 16, 1481.

S. MORGULIS

Researches on the bacteriocidal action of thorium emanations. J. CLUZET, A. ROCHAIX AND A. CHEVALLIER. *Compt. rend. soc. biol.* 88, 510-2(1923).—Considerable doses of Th emanation are required even to diminish the vitality of microbes. Sterilization can be obtained but the dose is greater than that necessary to kill a guinea pig.

S. MORGULIS

Researches on the action of adrenaline on pneumococci. ELENA PUSCARIU AND I. NITZULESCU. *Compt. rend. soc. biol.* 88, 540-1(1923).—0.5 mg. of adrenaline per 1 cc. of bouillon does not check the development of pneumococci. In another series of expts. a drop of a 24-hr. culture was dild. with 2 cc. of water contg. variable amts. of adrenaline. This was incubated for 12 hrs. at 37° and injected into rabbits. With 0.2-0.07 mg. of adrenaline the pneumococci did not grow, while in the controls where only water was used or even with 0.05 mg. adrenaline an abundant growth was obtained.

S. MORGULIS

Typhoid bacilli and catalase. H. VINCENT. *Compt. rend. soc. biol.* 88, 590-1(1923).—A suspension of the bacilli in physiol. salt soln. shows increasing catalase activity with time. The amt. of  $H_2O_2$  is sometimes not decomposed entirely before many days have elapsed (as much as 60 days). This effect is attributed to the setting free of catalase by autolysis, and this can be greatly hastened when the suspension is kept at 38° instead of at room temp. Cultures made in collodion bags differ from the ordinary culture in that they show the greatest catalase activity in the beginning and this in the course of a few hrs. disappears.

S. MORGULIS

Action of dilute acids in blood cultures. I. W. HALL. *J. Path. Bact.* 25, 297-304(1922).—Blood cultures may be accelerated by the addn. of sufficient lactic or nitric acids to adequately buffered nutrient broth to render the medium  $1/100$  N. It is possible to plate and identify within 24 hours. This will not alter the  $p_H$  more than 0.1. The comparison of growth in simple broth and in acid broth gives an insight into the resistance of the patient.

JOHN T. MYERS

Use of metallic salt emulsions. PAUL SAXL. *Med. Klin.* 19, 57-9(1923).—When tested for germicidal action against *B. coli*, emulsions (in serum) of the chlorides of Ag and Hg are almost as efficient as are solns. of the salts having the same concn. of Ag or Hg. Emulsions of these salts are non-irritating to the skin, mucous membranes, or wound surfaces.

G. H. S.

The Gram-staining relations of the intestinal bacteria of infants, and their depen-

dence upon the type of nourishment. W. STOYE. *Z. Kinderheilk.* 33, 313-28(1922).—The reaction of bacterial types under diff. nutritional conditions to their Gram-staining suggests that the reaction is to be referred to purely chem. properties; shades and degrees of staining may be associated with phys. properties. Gram-positiveness is associated with the lipoid content of the bacteria, particularly with the content of free fatty acids, fats and waxes. Gram-positive organisms might be termed lipophil. The multiplication of Gram-positive bacteria in the intestinal tract of infants is favored by the addn. of fats and certain carbohydrates, particularly lactose, to the diet. The amt. and nature of the fatty acids and soaps in the intestine det. the relative abundance of Gram-negative and Gram-positive bacteria. G. H. S.

New derivatives of quinine [their bactericidal action] (HEFFTER) 17.

BITTING, K. G.: Effects of Certain Agents on the Development of Some Moulds. Monograph published by the Glass Containers Assoc. of America, 70 Fifth Ave., New York City. 54 pp.

CHRISTIANSEN, MAX: Le bacille de la diphtérie. Reactions serologiques, fermentations, influence de la concentration des ions hydrogenes, virulences, etc. Classifications en types. Paris: Octave Doin. 208 pp.

## D—BOTANY

B. M. DUGGAR

Distribution of pentosans in the corn plant at various stages of growth. J. H. VER HULST, W. H. PETERSON AND E. B. FRED. *J. Agr. Research* 23, 655-63(1923).—Golden Glow corn was grown in a greenhouse and at different periods pentosans and methylpentosans were detd. in various portions of the plants. The pentosans varied from 7.4% in the kernel to 31.8% in the cob at maturity. During the 1st 30 days after planting the wt. of pentosans increased from 2.2 to 4.1 g. per 100 plants, although there was no increase in dry material. Only 0.37% of methylpentosans was found. Addns. of rhamnose to the corn tissue were made and the wts. of phloroglucide sol. in hot EtOH were approx. equal to those obtained from both rhamnose and corn tissue separately. Free pentosans varying from 0.6 to 1.7% of the dry matter were present in the corn plant throughout its period of growth. A destruction of the pentosans of green corn stover was obtained by pure cultures of a no. of organisms, the max. being 12.8% by a cellulose fermenter, *B. flavigena*. F. C. COOK

Accumulation of aluminium and iron compounds in corn plants and its probable relation to rootrots. G. N. HOFFER AND R. H. CARR. *J. Agr. Research* 23, 801-23(1923).—Sol. salts of Al, Fe and Ca, also various acids were injected into cornstalks and the data recorded. A definite cumulative toxicity was established and it is believed that the same phenomenon takes place in the field. Fe and Al accumulate in the vascular plate tissues in the nodes of the stalk and shank and the scutellum of the kernels. The metals also concentrate in the tissue. The ash of cornstalks from different localities varied from 3 to 6.3%. The  $Al_2O_3$  averages 1.99% in 8 healthy stalks and 3.73% in 21 diseased stalks. The most severe cases of rootrot have been found in soils notably deficient in available Al and Fe salts. Abundant Al injury in corn plants in certain fields is an indication of deficient available phosphates. The application of CaO and phosphates to soils showing rootrots has a beneficial control action. In some cases the use of limestone alone proved harmful but in all cases applications of available phosphates produced better plants and plants more resistant to rootrots. F. C. COOK

A preliminary note on the constituents of *Pogostemon parviflorus*, Benth. D. B. LIMAYE. *J. Proc. Asiatic Soc. Bengal, Proc. 8th Indian Sci. Cong.* 17, cxxix(1921).—A cryst. substance has been obtained by distg. the leaves of *Pogostemon parviflorus*, Benth. with steam, the mean yield being 0.11% on the green leaves. The substance m. 107-8° and a 10% soln. in alc. gave a rotation of +14° in a 1 dm. tube. Analysis leads to the formula  $C_{10}H_{14}O_2$ , but the substance has not been identified with any known compd. It yields a dibromo deriv. m. 104-5°. The name "Pangli Camphor" is suggested. E. J. C.

Origin of essential oils in living plants. CHAS. SIMPSON. *Perfumery Essent. Oil Record* 14, 113-9(1923).—An attempt is made to indicate in order the probable natural processes involved in the formation of the so-called "essential" oils. W. O. E.

The physiology and biology of excretions. ERNST STAHL. *Flora* 113, 1-132(1919); *Botan. Abstracts* 11, 677.—With the disappearance of nitrates in many plants there is an increase in the Ca oxalate content. The supplying of org. and inorg. Ca compds. to *Dianthus* and other plants causes them to form oxalic acid continuously.

Ca is inactivated through combination with other acids. The importance of the watery excretions of the plant lies in the field of salt economy. Plants with a large amt. of excretion show a rapid growth and are autotrophic, whereas plants lacking guttation are slow-growing and very often are mycotrophic. A function of the hydathodes may also be to rid the plant of certain substances which may cause injury if allowed to accumulate. The state of stomatal opening has a direct relation to nyctinastic, hydro-nastic, and chemonastic movements. The substances remaining after evap. the guttation liquid to dryness always contain ash substances, often with large amts. of org. substances. Extra floral nectaries also excrete ash substances as well as sugars. In many cases there seems to be a certain relation between the ash content of a plant and the excretory ability. Those plants which secrete freely have a low ash content while those lacking the power of secretion (*Chenopodium album*) have a high ash content. There seems to be a relation between guttation and crystal formation. Plants with a large amt. of excretion show little crystal formation, whereas those with a large amt. of crystal formation show little or no guttation. There seems to be a relation between secretory activity and the type of protection against animal feeding. Thorns and spines are found mainly on plants with limited or no excretory activity. Plants (*Equisetum*, grasses) with an active guttation show a protective covering of silicates. Many leaves cease their excretory activity when they change position. This cessation of guttation is probably bound up with factors influencing transpiration. There is a certain relation between guttation and pollen production. The Rosaceae with prolific pollen production are characterized by a heavy guttation, while the Papilionaceae with a limited pollen production are slow-growing and show little or no guttation.

H. G.

**A theory of carbon dioxide assimilation.** OTTO WARBURG. *Naturwissenschaften* 9, 354-8(1921); *Botan. Abstracts* 11, 288; cf. *C. A.* 16, 3670.—The question as to how the substances taking part in the process of assimilation in the living cell gain the power of reaction is answered by W. with his theory that these substances are absorbed by heavy metal-contg. surfaces of the solid cell substances and thus activated. Any destruction of the surface of these heavy metal-contg. particles results in the destruction of the place of the reaction and therefore the ability to assimilate is lost until the surfaces are restored. The existence of this surface and heavy-metal catalysis is then discussed and the factors which influence these catalytic processes resulting in assimilation are pointed out in detail.

H. G.

**Effects of nitrate of soda on the nutrition of the tomato.** PAUL WOKK. *Proc. Am. Soc. Hort. Sci.* 17, 138-46(1920); *Botan. Abstracts* 11, 124.—Young plants in greenhouse soil have the highest N content. Plants in active growth exhibit a N content above 0.3% whether treated with 256 or 8 g. of nitrate. (3) Low N treatment "gave external evidence of advanced starvation, while intermediate figures were associated with plants that seemed to have entered upon such a decline." That excessive nitrate applications were osmotically injurious rather than poisonous was indicated by more pronounced wilting, stunting, and blossom end rot during the summer. The latter trouble was checked when the water content of the sand was increased. There was a range in carbohydrate content from 0.92 to 5.97%. "High carbohydrate content occurs in most but not all starved plants. The range from 0.92 to 3.66% seems to show plants in all categories of vegetation, fruitfulness, and N content. Thus, barring the starved sets, there appears to be little if any correlation between this factor and plant performance." W. draws special attention to the desirability of analyses of successive samples from the same plants.

H. G.

**Nitrogen reserve in apple trees.** R. H. ROBERTS. *Proc. Am. Soc. Hort. Sci.* 18, 143-5(1921); *Botan. Abstracts* 11, 684-5.—A N reserve can be accumulated and utilized by apple trees. Strongly vegetative trees made an excellent growth when transferred to a nutrient medium low in N. Chem. analyses of 2-year wood showed a decrease of N content of such trees. Analyses also showed an accumulation of N in trees which were maintained in, or transferred to a high N nutrient. Carbohydrate compds. decreased with an increase in N content and increased with a decrease in N content. Little or no blossom-bud formation occurred under conditions of either high or low N content, but abundant formation occurred with an intermediate N content when, likewise, the carbohydrate content was intermediate.

H. G.

**Extraction and separation of the pigments of *Nereocystis luetkeana*.** GRACE E. HOWARD. *Publ. Puget Sound Biol. Sta.* 3, 79-91(1921); *Botan. Abstracts* 11, 298.—It is possible to ext. chlorophyll *a* and *b*, carotin, xanthophyll, and fucoxanthin, following the general processes used by Willstätter, but it seems impossible to do this with pure solvents. When put into a colloidal state the chlorophyll carries a negative charge.

Mg proved to be present in chlorophyll; and there is good evidence of the presence of chlorophyllase in kelp. H. G.

**Formation of vitamin A in plant tissues.** II. K. H. COWARD. *Biochem. J.* 17, 134-44 (1923).—The technic has been described in previous papers (Drummond and Coward, *C. A.* 15, 252, 4021). Using wheat, C. finds that "the amt. of vitamin A is increased considerably by exposing the seedlings to sunlight." Elec. light is also effective in increasing the rate of formation of vitamin A. The presence of CO<sub>2</sub> in the surrounding atm. has no influence; neither does the absence of O<sub>2</sub> in the surrounding air prevent the growth of this vitamin. "The almost complete absence of Ca salts from the nutrient soln. of a water culture of *Tradescantia* does not prevent the formation of vitamin A in the leaves of the plant." BENJAMIN HARROW

**Notes on the chemistry of certain Australian plant products.** I. H. G. SMITH. *J. Proc. Roy. Soc. N. S. Wales* 56, 180-4 (1922).—(1) Leaves of *Acacia verniciflua* obtained from Eden, N. S. Wales, were found coated with a resin consisting of resin acids and neutral resins in approx. equal proportions. Resin is an unusual constituent in members of the order Leguminosae. (2) *Baeckea Gunniana* was obtained in March at Mt. Kosciuszko, N. S. Wales, for distn. of the essential oil, which amounted to 0.214%. It had an unpleasant odor resembling certain terpenes. Nearly 50% consisted of dextro-rotatory pinene, while the less volatile fraction was composed largely of a sesquiterpene; cineole was also present in small amt. The crude oil had a sp. gr. of 0.9172, [ $\alpha$ ]<sub>D</sub> + 8.4° and  $n_D$  1.4856. 46% distd. at 153-70°, 26% at 170-200° and 18% at 240-65°. After redistn., the 1st fraction yielded a nitroso chloride m. 103-4°, indicating the terpene to be pinene. Cineole amounted to 9% of the crude oil. (3) *Sarcostemma australe*, order Asclepiadaceae, known as caustic vine or caustic plant, was collected in Central Australia. The leafless pea-green stems were coated with a silvery bronze-like material contg. a fair amt. of wax. The central pipe-like stem, when freshly cut, was filled with a delicate fibrous material through which latex traveled. The mass, coagulated from latex with AcOH, amounted to about 16% of latex. The actual rubber, after having been treated with C<sub>2</sub>H<sub>5</sub>O and CHCl<sub>3</sub>, amounted to about 7% of latex. It was elastic although somewhat soft and had all the properties of rubber.

H. C. PARISH

**Proteolipoid nature of sterinoplasts of the white lily.** MARCEL MIRANDE. *Compt. rend.* 176, 596-8 (1923).—A microscopical study showed that the central body of the sterinoplasts is of lipoidal nature. The covering consists of a thin outer protein layer and an internal thicker layer formed of protein material in granular concentric striae united by lipoidal material. This is limited internally by a thin granular skin of proteolipoidal compn. The entire internal layer is dislocated by dissolution of the lipoidal gang and its proteic debris remains in the external protein skin which remains intact. L. W. RIGGS

**Modification of the alkali salt absorption of living plant cells by multivalent cations.** HANS NETTER. *Arch. ges. Physiol.* (Pflüger's) 198, 225-51 (1923).—The salts of the bivalent cations inhibit deplasmolysis of *Rhoeo discolor* in weakly hypertonic NaCl soln. The order of effectiveness is Ca > Ni > Co > Sr > Ba > Mg > Mn. Salts of heavy metals inhibit salt absorption and perhaps water absorption also, reacting upon the plasma surface, inducing contraction and sudden deplasmolysis by bursting. These effects do not take place with the weakly inhibiting Mn. In high concns. Mg causes deplasmolysis. The alk. earths do not react with the plasma membrane or injure the protoplasm, but they inhibit salt absorption. G. H. S.

**Osmotic pressure and protoplasmic flow in plant cells.** P. J. JURISIC. *Z. allgem. Physiol.* 20, 100-10 (1922).—In agreement with Ewart it is concluded that the 1st phases of protoplasmic streaming take place without any alteration in the osmotic pressure, and it also appears that the secondarily produced streaming takes place without any reference to the osmotic pressure or to changes in pressure. In plant tissues the osmotic pressure increases for a time and then diminishes; the protoplasmic flow shows no parallel changes. G. H. S.

**Chemical constituents of green plants. XXII. The occurrence of succinic and oxalic acids in currants (*Ribes rubrum*).** H. FRANZEN and F. HELWERT. *Z. physiol. Chem.* 124, 65-74 (1923).—In the filtrate from the Pb ppt. of currant juice succinic, malic and citric acids were found. Unsaturated acids are also present in small aunts. Oxalic acid appeared to be present in traces, but lactic acid is probably absent. R. L. STEHLE

**The determination of phosphoric acid in plant ashes (KYULYUMOV) 7. Note on *Boletus cervinus* (REEB) 17. The reduction of carbon dioxide by ultraviolet light (SPOHR) 3.**



## E—NUTRITION

PHILIP B. HAWK

## NORMAL

**The influence of war nutrition upon tuberculosis mortality.** HANS FUTTER. *Beitr. klin. Tuberk.* 51, 202-10(1922).—A comparison of the tuberculosis mortality increase and the body weight decline figures showed a marked correlation. H. J. C.

**The energy consumption of Australian students.** H. S. H. WARDLAW. *Med. J. Australia* 2, 294-300(1922); *Australian Sci. Abstracts* 1, 29.—Analyses of a day's food of 19 University students and teachers showed the following av. weights of the different substances consumed. For ten men subjects: total food 448.2, fat 74.9, carbohydrate 265.8, protein 94.1, ash 13.5 g. For nine women subjects: total food 392.1, fat 71.2, carbohydrate 245.9, protein 63.6, ash 11.8 g. The av. daily energy content of the food was 2170 calories for the men subjects, and 1925 calories for the women subjects.

H. G.

**Association of vitamin A with the lipochromes of plant tissues.** K. H. COWARD. *Biochem. J.* 17, 145-56(1923).—Lipochromes are present in many plant tissues before the appearance of vitamin A. "A comparison between the abs. amts. of lipochrome in shoots which will not promote growth and those which do so once again proves that the activity of the tissue is not measured by its lipochrome content." B. H.

**Ingested fat and body fat as precursors of the acetone bodies.** R. S. HUBBARD. *J. Biol. Chem.* 55, 357-63(1923).—The subject received a diet furnishing 1,800 cal. of which 10% was protein, 10% carbohydrate and 80% fat for 6 days, a diet low, but not extremely low, in antiketogenic material and high, but not extremely high, in fat. From the 7th to the 9th day the fat was left out of the diet with the expectation that the fat withdrawn would be replaced by an approx. equiv. amt. of body fat. On those days when fat was omitted from the diet the same amts. of  $\text{Me}_2\text{CO}$  were excreted as when it was included indicating that under the conditions of the expts. tissue fat and ingested fat give rise to equal amts. of the acetone bodies. The amts. of acetoacetic and  $\beta$ -hydroxybutyric acids were also unchanged when the diet was altered. No changes were observed in the amts. of fat and cholesterol in the fasting blood under the two conditions. The diet fed was such as should have caused no increased excretion of  $\text{Me}_2\text{CO}$  according to Shaffer's formula but the small increases which occurred could be attributed to variation in the mixts. of foodstuffs burned at different times during the day and in different parts of the body.

A. P. LOTHROP

**Studies in uric acid metabolism. III. The influence of fats and carbohydrates on the endogenous uric acid elimination.** H. B. LEWIS AND R. C. COTLEY. *J. Biol. Chem.* 55, 373-84(1923); cf. *C. A.* 12, 2607.—The hourly rate of uric acid elimination was not influenced by the ingestion of fat (cream) up to 135 g. by a fasting individual who has previously been on a purine-free diet low in protein. Ingestion of 50 g. of glycerol caused a marked increase during the 2nd and 3rd hrs. but amts. equiv. to the glycerol contained in the fat fed exerted no influence. The ingestion of fat previous to administration of glycozell did not affect the stimulating action of that amino acid. Moderate amts. (100 g.) of lactose, sucrose or glucose did not influence the uric acid excretion but amts. of honey or com. glucose sirup greater than 200 g. caused an increase which, however, was neither so const. nor so marked as with glycerol or amino acids. The results apparently support the theory, previously advanced (*C. A.* 12, 2607), that "the increases in the output of endogenous uric acid following the ingestion of non-purine foodstuffs are due, in part at least, to a general stimulation of cellular metabolism, occasioned by the presence of the foodstuffs of their products of catabolism in the cells."

A. P. LOTHROP

**Studies on yeast. V. The vitamin B content of yeast.** V. G. HELLER. *J. Biol. Chem.* 55, 385-98(1923).—Studies were made of the vitamin B potency of the yeast, *Saccharomyces cerevisiae*, Fleischmann's Race F; 2.5% of this yeast is sufficient for normal growth and reproduction is possible at this level but is hardly normal although young may be brought to maturity. Slightly better than normal growth results when 5% is used and normal young are obtained and weaned although, shortly before the weaning time, the young do not develop as normal young should. Drying of the yeast destroys some of the vitamin. It is not as rich in vitamin B when grown in a synthetic medium as when grown in wort. This yeast not only synthesizes the growth-promoting vitamin but the antineuritic vitamin as well as shown by its power to cure polyneuritis in pigeons.

A. P. LOTHROP

**Vitamin B. I. A modified technic in the use of the rat for determinations of vit-**

amin B. H. STEENBOCK, MARIANA T. SELL AND E. M. NELSON. *J. Biol. Chem.* 55, 399-409(1923).—"When rats are prevented from supplementing their diet by the consumption of excreta the vitamin B content of the exptl. rations must be at least twice as high. This narrows down the margin of safety in the ability of the ordinary grains to furnish the rat with a sufficiency of the vitamin for max. growth; it appears that in the neighborhood of 60% of the ration must be grain to accomplish this purpose." Because this fact has not been taken into consideration it is evident that many of the detns. of vitamin B recorded in the literature are worthless. In detns. of vitamin B the rats should be kept in cages provided with a false screen bottom 3 meshes to the inch.

A. P. LOTHROP

Vitamin B. II. Storage of vitamin B by the rat. H. STEENBOCK, MARIANA T. SELL AND J. H. JONES. *J. Biol. Chem.* 55, 411-9(1923).—"When young rats of different ages are put on a ration contg. little or none of the vitamin B they are able to maintain life for about the same length of time. However, within certain limits, the older and larger the rat the greater the loss in wt. before death results. Whether this indicates a need of more vitamin on the part of the larger animal or merely a more disastrous effect of corresponding depletion is not clear. When young rats reared to 23-25 days of age on rations of doubled or quadrupled vitamin B content are subsequently put on a ration contg. little or none of the vitamin B they continue to live for the same length of time, but those which previously received generous amts. of vitamin gain in wt. more before decline sets in. When young rats are continued until 32 days of age on high vitamin B rations, maintenance of life is not prolonged, but one fact is emphasized and that is, that after having been on such ration a greater gain in wt. results before failure ensues. All the evidence points to little ability on the part of the rat to store vitamin B." The animals were prevented from supplementing the vitamin B content of the rations by the consumption of excreta by being kept in cages provided with false screen bottoms 3 meshes to the inch.

A. P. LOTHROP

The nutritive properties of milk with special reference to reproduction in the albino rat. II. H. A. MATTILL AND N. C. STONE. *J. Biol. Chem.* 55, 443-55(1923); cf. *C. A.* 14, 3701.—"On rations in which all the protein and vitamins were supplied by varying proportions of dry milk, rats (32 males and 22 females) grew at a rate above the normal up to about 75 days of age. Thereafter the rate fell below normal, the decline in females being more rapid than in males. At 175 days females were 14% underweight and males 5%. Rations contg. 50, 60, and 70% of dry milk were more favorable than those of 100%. Reproduction was not successful on any of the rations and a change to rations contg. added protein-free milk, cod-liver oil, traces of KI, or even to stock rat food did not restore reproductive function. Mating tests with fertile stock animals showed that milk-fed females were sterile, the males not always so although the offspring did not live. On milk rations (60%) contg. 5% dry yeast, 8 of 9 females produced 14 litters sired by males on the same ration; none of the young lived. One litter sired by a male on stock rat food did live. The success which other investigators have had in rearing two or more generations on all milk rations cannot now be explained except by assuming that the colony of rats is lacking in vigor and therefore responds more promptly to unfavorable circumstances." In male rats the gradual decline in reproductive function becomes complete at about 200 days of age; the testes shrink to about half their normal size and show the appearance of degeneration resulting from the absence of H<sub>2</sub>O-sol. B. The addn. of yeast does not appear to modify this degeneration. The sterility of the females cannot be explained by decline in ovarian function since the ovaries histologically appear normal although they were only about 1/2 their normal wt. Ovulation seemed to be taking place frequently. The influence of yeast, if any, on uterine function remains to be detd. The added vitamin B thus supplied failed to achieve normal lactation.

A. P. LOTHROP

Vitamin B and the gonads. H. GOTTA. *Compt. rend. soc. biol.* 88, 373-5(1923).—Pigeons were fed either a diet free from vitamin B or one to which yeast was added. A comparison of their organs shows a certain difference in wt. of the liver, kidney, and heart in the 2 sets, those of the latter being heavier. The greatest difference, however, is in the wts. of the testes and ovaries which are several times smaller than those from pigeons provided with yeast. The testes of pigeons deprived of vitamin B are also atrophic with definite signs of degeneration of the seminal epithelium. S. M.

Effect of parenterally administered vitamin A on growth. E. WOLLMANN AND M. VAGLIANO. *Compt. rend. soc. biol.* 88, 336-8(1923).—Vitamin A has practically the same effect upon growth whether it is given by mouth or parenterally, except that in the latter case its action may be delayed owing to slower absorption. S. M.

Basal metabolism in Buenos-Aires. A. SORDELLI. *Compt. rend. soc. biol.* 88,

389-90(1923).—The basal metabolism is the same as that found for men in other parts of the world. S. MORGULIS

**Influence of the chlorides in the diet on the urinary acidity.** R. FONTAINE. *Compt. rend. soc. biol.* **88**, 452-6(1923).—The acidity of the urine increases under a chloride-free regime. It is thought that the increased acidity exerts a diuretic action which is very significant when the diet is lacking in Cl. S. MORGULIS

**Variations in glucemia of a normal person under the influence of fats and proteins.** H. LABBÉ AND B. THEODORESCO. *Compt. rend. soc. biol.* **88**, 484-6(1923).—Ingestion of 50 g. of olive oil produces a diminution of the blood sugar content, which is not observed when either 50 g. of beer or 200 g. of meat are taken. When glucose is taken simultaneously with 50 g. of oil on the empty stomach the blood sugar curve is different from that obtained with a similar amt. of sugar alone in that the curve does not reach such a high peak and returns to the normal level sooner in the former case. S. M.

**Can pyruvic acid completely replace carbohydrates in a synthetic balanced ration?** E. AUBEL. *Compt. rend. soc. biol.* **88**, 667-9(1923).—When fat is substituted isodynamically for the carbohydrates of a balanced ration it is not possible to obtain N equil. in the exptl. rats. On adding increasing quantities of Na pyruvate to such a diet deficient in carbohydrates it is still impossible to get N equil. On the contrary, if the diet is completed with Na pyruvate but also contains a very small amt. of carbohydrate (sucrose) it becomes possible to obtain N equil. These expts. seem to call into question the importance attributed to this keto acid in the intermediary carbohydrate metabolism; they also point to the sp. need for carbohydrate in the organism. S. MORGULIS

**Effect of atropine on pigeons fed on a polished rice diet.** F. ARLOING AND A. DUFOUR. *Compt. rend. soc. biol.* **88**, 774-5(1923).—Repeated injections of atropine sulfate to the total amt. of 3-6 mg. facilitates and induces the appearance of the phenomena accompanying a diet of decorticated rice. Even while the atropinization is continued the pigeons are rapidly cured of the disease if they are placed on a normal diet. **Action of pilocarpine on pigeons under experimental inanition.** *Ibid* 775-6.—Pilocarpine also induces the appearance of the starvation symptoms in pigeons fed on decorticated rice about as rapidly as atropine, and the administration of this substance does not prevent quick recovery from the symptoms when the diet has been corrected. S. MORGULIS

**Experimental rickets.** H. SIMONNET. *Bull. soc. hyg. aliment.* **11**, 88-111(1923).—A review with bibliography. A. PAPINEAU-COUTURE

**Experimental rickets.** PAPPENHEIMER. *Gaz. hebdom. sc. med. Bordeaux* **43**, 567(1922); *Bull. soc. hyg. aliment.* **11**, 122-4(1923).—A series of lectures. A. P.-C.

**Investigations on experimental rickets: injurious effects of deficient diets: effect of ultraviolet rays on disturbances so caused.** ALLENBACH AND RENÉ SIMON. *Rev. hyg. soc. Strasbourg* **81**, 670(1923); *Bull. soc. hyg. aliment.* **11**, 124(1923).—Three groups (6 each) of young albino rats were fed: (1) normal diet, (2) McCollum's diet No. 3143 (*C. A.* **15**, 3667) rich in Ca and low in P and in fat-sol. vitamins, and (3) same as (2) but exposed daily to ultraviolet light. After 49 days group (1) was much bigger and heavier than (2) and (3), the latter two being practically the same. Radiophotographs showed in (2) and (3) enlargement of the cartilage but no well defined deformation of the bones. A. PAPINEAU-COUTURE

**The work of Pasteur in relation to nutrition.** DE POMIANE POZERSKI. *Bull. soc. hyg. aliment.* **11**, 135-60(1923).—An address. A. PAPINEAU-COUTURE

**Study of the comparative value of different parts of wheat grain.** MAURICE MIGNET. Thesis, Lyon 1920; *Bull. soc. hyg. aliment.* **11**, 190(1923).—Four pups from the same litter were fed, resp. 4 kinds of flour extd. from a soft wheat: (1) 55% extn.; (2) 80% extn.; (3) whole wheat; and (4) 80% extn. to which was added 5% of germ contg. 29% embryo and 22% protein. The daily diet per kg. was: milk 20-25 cc., bread the prepd. from above flours and 0.40% NaCl 40-50 g., raw dandelion 10 g., water *ad lib.* The increase in wt. after 80 days was 43.02, 48.49, 68.86 and 85.07%, resp. No. 1 showed evident signs of rickets, especially in the forelegs, which were decidedly curved. Special importance is attributed to the function of the mineral salts in the flour. The embryo and proteins are more active when mixed with smaller amts. of indigestible pericarp. A. PAPINEAU-COUTURE

#### ABNORMAL

**Vitamins and obesity cures.** GEORG ROSENFELD. *Centr. Inn. Med.* **44**, 18-20(1923).—Patients put on diets for the cure of obesity developed symptoms of disturbances of the nervous systems which are attributed to a deficiency of vitamins, presum-

ably of fat-sol. A. These symptoms were relieved by the administration of an ext. of carrots. Since this ext. contains both fat-sol. A and H<sub>2</sub>O-sol. B it cannot be certain which one is responsible for the relief obtained.

JULIAN H. LEWIS

**Undernutrition and internal secretion.** T. W. TALLQVIST. *Acta med. Scand.* 56, 640-57(1922).—The dietary deficiency during the last years of the war and subsequent blockade is regarded not as a qual. (vitamin) but as a quant. one, i. e., insufficient calories. The principal disease associated with this low calorie diet was the edema accompanied by hypotension and bradycardia. The edema is regarded as resulting from an increased permeability of the capillaries. The disease is thought to be of endocrine origin and to be due to a combined action of a hypothyroidism and hypoadrenalism. This is based on autopsy findings which have revealed that the thyroid in these edema patients was reduced to  $\frac{1}{2}$  its normal size. This effect on the thyroid is also used to interpret the fact that during these years of chronic undernutrition there has been a very decided falling off in cases of Basedow's disease. The widespread occurrence of achylia gastrica is attributed likewise to some glandular disturbance resulting from poor nourishment though the connection is not clearly recognized.

S. MORGULIS

**Undernutrition and disturbances in the internal secretion.** HANS CURSCHMANN. *Acta med. Scand.* 57, 240-7(1922).—Corroborates Tallqvist's findings but does not consider that the achylia was a general undernutrition effect.

S. MORGULIS

**The nitrogen-minimum in diabetics.** K. PETRÉN. *Acta Med. Scand.* Suppl. III, 101-12(1922).—P. obtained N equil. in diabetics with less N than the lowest amt. recorded for normal individuals (0.18 g. per kg.) by physiologists. This was accomplished even with small quantities of carbohydrates in the diet which, however, contained large amts. of fat. These studies show thus that fats also function as effective protein spacers. P. further found that by introducing days with a pure fat diet the N elimination in the urine could be diminished more than by fasting. The problem of dietetic treatment of severe diabetes. *Ibid* 112-34(1922).—A critic of the Allen starvation treatment, for reducing the sugar in blood and urine. A diet with a min. N, low carbohydrate and large amts. of fat is effective in bringing the blood sugar to a normal level, in actually improving the carbohydrate tolerance and reducing the excretion of acetone bodies even in severe cases of diabetes. The advantage of this diet over fasting is this: in fasting the acidosis is the result of a lack of carbohydrate which is counteracted by the reduction in N metabolism which tends to diminish the acidosis; with P.'s diet the advantage from a low N metabolism is attained even to a greater degree than by total fasting and its effect is not counteracted by a deficiency of carbohydrate in the metabolism, hence its greater efficacy in overcoming acidosis.

S. MORGULIS

**The blood of rats deprived of vitamins.** H. DAMIANOVICH, A. BIANCHI and LILIA A. SAVAZZINI. *Compt. rend. soc. biol.* 88, 377-8(1923).—A lack of vitamins A or B brings on quickly a condition of anemia which gradually grows more serious. Vitamin B deficiency produces this effect more rapidly and in a stronger degree. The administration of vitamin, especially vitamin B, ameliorates the condition.

S. M.

**Influence of certain carbohydrate foods on the blood sugar in normal and diabetic men.** C. BONORINO UDAONDO and M. CASTRIGYS. *Compt. rend. soc. biol.* 88, 392-3 (1923).—In the order of their increasing effect in causing hyperglucemia foods are arranged as follows: oats, potatoes, rice, bread and glucose.

S. MORGULIS

**The bone marrow in deficiency diseases.** G. M. FINDLAY and R. D. MACKENZIE. *J. Path. Bact.* 25, 402-3(1922).—Rats which have survived for a long time a diet deficient in vitamin A show an almost complete replacement of the hemopoietic tissue by fibrous tissue. On a diet deficient in vitamin A there is a considerable diminution in leucoblastic cells. If vitamin C is deficient, there are patches of gelatinous degeneration and fibrous tissue overgrowth throughout the bone marrow with disappearance of blood-forming cells. Rats fed on a diet contg. only a third of the normal protein but otherwise complete show hemorrhagic areas in the bone marrow with disorganization of hemopoietic cells.

JOHN T. MYERS

ELLIS, CARLTON and MACLEOD, ANNIE LOUISE: **Vital Factors of Foods, Vitamins and Nutrition.** London: Chapman & Hall, Ltd., 11 Henrietta St., Covent Garden, W. C. 2, 391 pp. 25s.

SLOVRZOV, B.: **Biochemistry of Partial Nutrition and of Hunger** (in Russian). Petrograd: Gosisdats. 26 pp.

## F—PHYSIOLOGY

ANDREW HUNTER

Principle, curves, and tables of correction for calculating results in clinical basal metabolism measurements. \* H. JANET. *J. physiol. path. gen.* 20, 366-75(1922).—The paper presents no new features.

A color reaction of urines with sulfosalicylic acid. E. CAVAZZANI. *J. physiol. path. gen.* 20, 467-71(1922).—A certain no. of urines develop a color, pink to violet, some hrs. after treatment with sulfosalicylic acid. This shows a band between D and E. It is insol. in  $\text{Et}_2\text{O}$ , sol. in amyl alc. Such urines show an increased content of Fe, the Fe compd. being apparently responsible for the color.

Functions attributed to the pituitary. I, II. J. CAMUS AND G. ROUSSY. *J. physiol. path. gen.* 20, 509-18, 535-47(1922).—Expts. on dogs and cats show that simple removal of the pituitary causes neither transitory polyuria, permanent diabetes insipidus, glucosuria, atrophy of the gonads nor the adiposogenitalis syndrome, while all of these can be produced by exptl. lesions of the base of the brain. Expts. are not sufficiently numerous to draw definite conclusions regarding skeletal development, infantilism, gigantism, and acromegaly.

The influence of the thyroid on the metabolism of man. E. GRAFE AND E. V. REDWITZ. *Mitt. Grenz. Med. Chir.* 36, 215-34(1923).—In hyperthyroidism, partial removal of the thyroid gland in man was followed by a permanently decreased metabolism. Partial removal of the normal-sized thyroid gland caused a temporarily decreased level of metabolism in some cases while in other expts. there was no change in energy output. These results show that partial excision of the thyroid can exert a considerable influence on heat production.

The problem of the inner secretion of the pancreas. J. WOHLGEMUTH AND T. KOGA. *Klin. Wochschr.* 2, 386-8(1923).—Blood normally contains a substance that mildly accentuates the hydrolyzing function of liver diastase. In well nourished dogs there is no appreciable variation in the concn. of this pancreatic hormone in the blood taken from different parts of the body. After 48 hrs. of starvation, however, the concn. of this hormone is markedly increased in the blood flowing from the pancreas to the liver. The deglycogenating effect of hunger upon the liver can, therefore, be explained as due to an increased activity of the liver diastase, due in turn to the hormone secreted by the pancreas in increased concns. under these conditions. The action of the liver diastase is probably reversible and the pancreas may, under proper conditions, secrete a second hormone capable of stimulating the synthetic function of the liver diastase.

Tethelin: A growth-controlling substance obtainable from the anterior lobe of the pituitary body. T. B. ROBERTSON. *Biochem. J.* 17, 77-82(1923).—The results obtained by Drummond and Canaan (*C. A.* 16, 1974) are "vitiating by a faulty method of prepn." "The statistical method of comparing the growth of normal animals with that of animals in receipt of dietary conditions must of necessity be superior to the haphazard method of comparing individual growth-curves or curves constructed from the growth of a few animals."

The effect of fat on the secretion of acid by the stomach. PAUL FRANK. *Wiener Arch. inn. Med.* 5, 591-604(1923).—Fat given with a meal either does not affect the secretion of acid by the stomach or increases the secretion of acid if the fat used is slightly decompd. Fat given before a meal slightly decreases the acidity of the gastric secretion. Permanent modification of the gastric acidity was not brought about by the repeated administration of small doses of fat.

The morphology of lipid substances in hunger. N. OKUNEFF. *Beitr. Path. Anat.* 71, 98-114(1922); cf. following abstr.—Rabbits were starved for various periods and the tissues examd. by stains and polarized light for anisotropic substances. The adrenal showed a slight increase in lipoids and the liver and spleen showed a marked increase. None of the other organs showed changes from normal. The findings were the same as those in hypercholesteremia after feeding cholesterol. The increased lipid substance consisted mainly of cholesterol esters.

Cellular changes in hunger. N. OKUNEFF. *Arch. mikroskop. Anat.* 97, 187-203(1923); cf. preceding abstr.—The changes which take place within the cells of the rabbit during hunger vary with the individual organ. Thus, in the liver and kidney the changes are of the simple atrophic or even of the destructive type. The changes in the pancreas indicate suppressed function; in the spleen there is an atrophy with an actual diminution of the total no. of cell elements.

Internal secretion between mother and fetus. ANDREAS TANBERG. *Acta Med.*

*Scand.* 56, 33-51(1922).—The thyroid glands of the fetus of goats deprived of their thyroids assume an early function. This does not happen when the mother's gland is intact. It is therefore evident that during fetal life the thyroid gland of the mother can act on behalf of the fetus, the thyroid substances passing through the placenta. It is also obvious from the expts. that the fetus with a functional thyroid cannot act on behalf of its mother.

S. MORGULIS

• Investigations on the distribution of chlorine between blood and tissues after charging the organism with sodium chloride, and some kindred problems. POUL IVERSEN AND HARALD HANSBORG. *Acta Med. Scand.* 57, 95-133(1922).—The deposition of Cl in the tissues during injection of a 10% soln. of NaCl takes place with such rapidity that a difference in the NaCl of arterial and venous blood can be demonstrated, an osmotic equil. between blood and tissues being established in a single circulation unless the injection rate is too great. The distribution of the Cl between blood and tissues is independent of the amt. injected, about 8% of the amt. always remaining in the blood. The NaCl is not evenly distributed in the organism's water, calcns. showing that there is usually considerably more NaCl in the blood than would correspond to its water content. After thyroidectomy the distribution may be altered, more NaCl being retained in the tissues than in normal conditions, and also contrary to what was found in the normal animal there remains less NaCl in the blood than would correspond to an even distribution of the salt over the total water content of the organism. Thyroidectomy thus seems to predispose to hydremia. Expts. with the use of diuretics or following ligation of the ureters show that the distribution of the salt injected is capable of being affected by renal secretion. Some time after the NaCl injection has been discontinued the curves of the percent of NaCl in arterial and venous blood cross, showing that the percent of salt in the tissues has become greater than that in the blood, and the evidence points to the renal secretion as the factor affecting this. In spite of the concn. of the blood there persists a violent diuresis which seems to depend on the osmotic pressure of blood as compared with that of tissues. When 1 or 2 kidneys are ligated, also when adrenaline or pituitrin is injected, the capillaries are so affected that more water passes from tissues to blood per unit of time than before ligation.

S. MORGULIS

Determination of the alkaline reserve of the cerebrospinal fluid. CH. O. GUILLAUMIN. *Compt. rend. soc. biol.* 88, 248-9(1923).—Using a titrimetric method of detn. the  $\text{CO}_2$  content of the cerebrospinal fluid of 5 adults was found on the av. 53%. Furthermore the  $p_H$  of the fluid and that of the blood are also in equil.

S. MORGULIS

Growth of embryonic guinea pig tissue cultures in media of different  $p_H$ . P. MENDELÉEFF. *Compt. rend. soc. biol.* 88, 291-3(1923).—Cellular growth depends directly upon the reaction of the medium and as the  $p_H$  becomes lower the proliferation of the tissue is improved.

S. MORGULIS

The physico-chemical conditions of the production of embryonic tissues. P. MENDELÉEFF. *Compt. rend. soc. biol.* 88, 293-5(1923).—The  $p_H$  value of the serum of pregnant guinea pigs was compared with that of embryos of different stages of development. The maternal serum was found to have a  $p_H = 7$ . The serum of very young embryos had a  $p_H = 5.8$ ; of  $3/4$  term embryos = 6; 3 hrs. after birth a  $p_H = 6.2$ ; 6 days after birth the  $p_H$  values of the serum attains the level of the mother.

S. MORGULIS

Influence of hypophyseal extract on the imbibition of water by tissues. A. BIASOTTI. *Compt. rend. soc. biol.* 88, 361-2(1923).—0.01 cc. of posterior lobe ext. is sufficient to increase the wt. of a frog 10%, while anterior lobe ext. has but little effect. The gain in wt. is due to imbibition of water. The muscles are pale and edematous.

S. MORGULIS

Influence of sleep on the elimination of the principal nitrogenous components. GEORGES FONTES AND ALEXANDRE YOVANOVITCH. *Compt. rend. soc. biol.* 88, 456-8(1923).—During the daytime there is a greater excretion of total and of urea N, a somewhat greater excretion of amino N, but a considerably smaller excretion of ammonia N than during the night. The percents of the different N components of the urine per 24 hrs. during the daytime and nighttime are, resp.: total N 54.0, 46.0; urea N 57.8, 42.2; ammonia N 38.4, 61.6; amino N 52.0, 48.0.

S. MORGULIS

Lipodiuresis in man. SICARD, FABRE AND FORESTIER. *Compt. rend. soc. biol.* 88, 564-5(1923).—An iodized oil contg. 0.54 g. of I per cc. was used. The substance was detd. in the daily urine by analyzing it for I after 5 cc. of the oil were injected into the cerebrospinal fluid, muscles, or trachea. In the first instance only 0.5% was recovered in the urine during 5 days; in the second instance 1.5%; but when the oil was introduced into the lung through the trachea as much as 22% appeared in the urine and the elimination was greatest during the first day, thus showing that lung tissue is particularly

active in producing lipodiuressis. X-ray examn. also corroborates these findings, the shadow thrown by the iodized oil persisting for months in the cerebrospinal fluid or muscles, but rapidly disappearing from the trachea. S. MORGULIS

**The in vitro production of hormones of the endocrine glands.** L. STERN AND F. BATTELLI. *Compt. rend. soc. biol.* **88**, 573-5(1923).—The authors had found that the finely macerated suprarenal capsule suspended in blood of its own species well provided with O and incubated at 37° continues to produce adrenaline. Similar expts. were made with the spleen which under similar conditions continues to produce lienin, a hormone causing hypertonicity of smooth muscle fibers. Positive results were also obtained with testicles. The results with pancreas deprived of digestive capacity by a preliminary ligation of the pancreatic ducts were not sufficient to draw definite conclusions, while the failure with hypophysis is attributed to the fact that these expts. were not made on fresh material but with glands obtained from the abattoir. S. M.

**Presence of carnisapidine in different animal tissues.** F. BATTELLI AND L. STERN. *Compt. rend. soc. biol.* **88**, 575-7(1923).—The name carnisapidine is applied to the substance which gives to bouillon its characteristic flavor. The comparison of the flavors of different tissues was carried out as follows: the ground tissue was put into 6 vols. of boiling water; the ext. was filtered and concd. to  $1/10$ - $1/20$  of its vol. This was then diluted until the flavor became scarcely perceptible, and 1 cc. of the liquid then represented 1 flavor unit. The results of numerous comparisons show that muscle, liver, kidney and spleen contain very great quantities of carnisapidine, the thymus, spinal cord and lungs small quantities, while the blood has no appreciable amt. S. M.

**Gastric leucopdesis and crystalloids.** M. LOEPER AND G. MARCHAL. *Compt. rend. soc. biol.* **88**, 598-9(1923); cf. C. A. **17**, 1663.—Migration of leucocytes into the gastric cavity occurs also when glucose, sucrose, NaCl or CaCl<sub>2</sub> are ingested. The great majority of the cells are polymorphs, but the proportion varies with the nature of the ingested material. With glucose 70%, with sucrose 75%, with NaCl 58% and with CaCl<sub>2</sub> 68% are polymorphonuclear leucocytes. S. MORGULIS

**The study of the changes in the blood during digestion.** L. HANNAERT AND ROBERT WODON. *Compt. rend. soc. biol.* **88**, 636-8(1923).—In the dog on an empty stomach there is present the same amt. of amino acid in both the general and in the portal circulation, but during digestion the quantity is increased in the portal blood. In the general circulation there are no polypeptides present either in the condition of fasting or of digestion, but in the portal circulation during digestion there is an appreciable amt. of polypeptides. The urea of the blood also increases very markedly during digestion and this is true for both the general and the portal blood. S. MORGULIS

**A contribution to the study of the reaction of arterial and venous blood.** E. J. BIGWOOD. *Compt. rend. soc. biol.* **88**, 639-42(1923).—The reaction of both arterial and venous blood is practically the same, the av. difference in  $p_H$  value being 0.028. In the pathol. alterations affecting the acid-base equil. the  $p_H$  value of both arterial and venous blood changes to about the same degree, the difference between them being 0.04 instead of the 0.02 under normal circumstances. S. MORGULIS

**The sarcochromogen content of different animal tissues.** F. BATTELLI AND L. STERN. *Compt. rend. soc. biol.* **88**, 679-81(1923).—B. and S. designate by the name sarcochromogen the coloring matter occurring in aq. exts. of tissues evapd. at a high temp. The greatest amts. were found in liver exts.; medium quantities in muscle and spleen exts.; the blood gave only traces of this substance. S. MORGULIS

**The fate of carnisapidine and of sarcochromogen in the animal organism.** L. STERN AND F. BATTELLI. *Compt. rend. soc. biol.* **88**, 681-3(1923).—Carnisapidine given to dogs either by way of the mouth or subcutaneously rapidly disappears, no appreciable amt. appearing in the urine even after 48 hrs. On the contrary, sarcochromogen disappears only when it is ingested; when given subcutaneously it comes out in the urine. It is thought probable that the substance accumulates in the liver where it is either retained or destroyed. S. MORGULIS

**Variations in the leucocyte count accompanying digestion. Relation to hepatic insufficiency and to the vago-sympathetic tone.** H. CLAUDE, D. SANTENOISE AND P. SCHIFF. *Compt. rend. soc. biol.* **88**, 686-8(1923).—Variations in the leucocyte level following a meal are conditioned by the functional state of the liver and of the vago-sympathetic tone. When one of these conditions is known the other can be appraised by a study of the digestive hemoclasia. This is supposed to be of value in the examination of the liver as well as in the exploration of the vegetative nervous system in various psychopathies. S. MORGULIS

**Relation between the calcium ion and the partial oxygen pressure in the frog heart.** A. GEORGIOU AND J. P. BOUCKAERT. *Compt. rend. soc. biol.* **88**, 970-2(1923).—A

reduction of the partial O pressure of the perfusing fluid has less effect on a heart receiving 360–480 mg. of  $\text{CaCl}_2$  per l. than with ordinary Ringer soln. When the  $\text{CaCl}_2$  reaches a concn. of 1 g. per l. a great diminution of the O tension fails to provoke injurious effects.

S. MORGULIS

**The optimum concentration of calcium in the frog muscle.** J. P. BOUCKAERT AND JAN BELEHRADEK. *Compt. rend. soc. biol.* **88**, 973–5(1923).—A muscle perfused with a Ca-free fluid goes into fibrillations and becomes edematous. It regains, however, its power of contraction when Ca is added to the perfusion liquid. The height of the contraction is a function of the Ca concn. of the fluid used. The  $\text{CaCl}_2$  of Ringer soln. does not represent an optimum concn., the latter being at a much higher level (0.84 g. per l.).

S. MORGULIS

**Effect of temperature on the rate of blood coagulation.** I. N. KUGELMASS. *Compt. rend. soc. biol.* **88**, 996(1923).—Arrhenius' factor for the coagulation at  $39^\circ$  is 13944 and at  $20^\circ$  13024. The temp. of  $39^\circ$  favors a greater degree of dispersion and this is thought to account for the fact that the pre-coagulation period is shorter at  $39^\circ$  than at  $20^\circ$ .

S. MORGULIS

**Muscular exercise, lactic acid, and the supply and utilization of oxygen.** A. V. HILL AND HARTLEY LUFTON. *Quart. J. Med.* **16**, 135–70(1923).—O is not used in the primary break-down processes of rest or activity, it is used only in what may be called recovery processes. Large amts. of lactic acid, up to 1.5 g. per kg. body wt., may be produced. If exercise is too great the supply of O cannot cope with the production of lactic acid and exhaustion results. The exhaustion following long continued moderate exercise is due to the diffusion of lactic acid out of the muscles where it is slowly oxidized and removed. Lactic acid in the body always appears as the lactate of Na, K, or  $\text{NH}_4$ . The rate at which chem. processes of recovery occur starts at a low level, rises to a max. and slowly falls to zero. The greater the initial effort the greater the relative rate of recovery.

JOHN T. MYERS

**Coefficient of stability of the blood structure.** GÉZA V. GERLOCZY AND FRANZ FALUDI. *Biochem. Z.* **135**, 153–64(1923).—From calcns. involving plasma viscosity, sedimentation velocity of the corpuscles, and the difference in density of corpuscles and plasma, a coeff. is arrived at. Detd. in a few bloods, differences in pathol. and normal conditions are significant.

GEORGE ERIC SIMPSON

**Action current, temperature, and latent period of striated muscle.** A. JUDIN. *Arch. ges. Physiol. (Pflüger's)* **198**, 263–6(1923).—Temp. has a marked effect upon the action current of the frog gastrocnemius, the oscillations becoming smaller and less evident as the temp. is reduced from  $30^\circ$  to  $3^\circ$ . The first oscillation is the one primarily affected. The latent period cannot be shorter than the duration of the first oscillation of the action current at a given temp. A certain chem. process must be completed after stimulation before contraction of muscle takes place.

G. H. S.

**Muscle hardness.** ERNST MANGOLD. III. Increase in hardness of muscle of cold-blooded animals in heat rigor and in rigor mortis, and their relation to muscle shortening. CARL DETERING. *Arch. ges. Physiol. (Pflüger's)* **198**, 279–88(1923); cf. C. A. **17**, 1056.—The methods applied by Mangold to mammalian muscle (rabbit) were used with frog muscle and the relationships found in the latter agree with those recorded for the muscle of warm-blooded animals. IV. Changes in hardness in stimulated muscle. E. MANGOLD AND C. DETERING. *Ibid* 289–96.—The changes in hardness of muscle (frog gastrocnemius and rabbit triceps surae) after tetany closely approximated the results obtained under other functional and exptl. changes in condition. The quant. agreement found for the maximal increase in hardness under various conditions of contraction and rigor suggests that there is a qual. similar mechanism in all. The development of muscle hardness and of muscle shortening are distinct processes and are apparently based upon distinct physico-chem. changes in condition in the tissue. V. Hardness changes in swelling, water removal and chemically contracted muscle, and their independence of length changes. TOMITARO INAOXA. *Ibid* 297–310.—Under the conditions indicated the alterations in hardness are quite independent of changes in length.  $\text{NH}_4$  and  $\text{CHCl}_3$  cause a change in the length of a muscle more quickly than they do in hardness. In swelling in  $\text{H}_2\text{O}$  the increase in hardness takes place more slowly but reaches a degree equal to that of  $\text{CHCl}_3$  or  $\text{Et}_2\text{O}$  rigor, but there is no significant shortening. The change in hardness in muscle subjected to 10%  $\text{NaCl}$  or  $\text{NH}_4\text{Cl}$ , to 5%  $\text{NaF}$ , to 0.05  $N$  lactic acid or 0.01  $N$   $\text{HCl}$  did not differ from the changes observed under other conditions, and the hardness bore no const. relation to the shortening. The substrate in which the process occurs is most probably the sarco-plasm.

G. H. S.

**Vital staining of connective tissue cells in fat resorption.** N. KUSNETZOWSKY.



*Arch. mikroskop. Anat.* 97, 32-47(1923).—When a colloidal dyestuff (trypan blue) is introduced into the circulation and another substance (egg yolk) is injected locally both the macrophages and the fibroblasts may absorb both. The fibroblasts show but little avidity for either substance and the absorption of fat does not appear to have any effect upon the fixation of vital stains by their protoplasm. The polyblasts (macrophages), on the contrary, have a great avidity and may become laden with the dye and the fat simultaneously. The amts. of the 2 substances taken up are variable and depend primarily upon the distance of the macrophages from the fat-lipoid masses deposited in the subcutaneous connective tissues. Cells in the immediate vicinity of the fatty substance take up the fats very energetically, and, as a result, lose almost completely their ability to ingest the dyestuff. Possibly all of the receptors of these cells have been satd. by fat, leaving no free affinities for the mols. of the dyestuff. Macrophages which are located at a certain distance from the subcutaneous fat-lipoid masses show the simultaneous ingestion of fat droplets and granules of stain. Thus, the greater the amt. of fat taken up by a single cell the less is the amt. of dye absorbed, suggesting that the receptors of the macrophage protoplasm unite most readily with that substance which is present in the greatest amt. in their environment. The nature of the affinity is not chem., but rather physico-chem., or perhaps purely phys.

G. H. S.

**Iron deposition and vital staining with carmine in rabbits.** F. J. MCGAY AND J. R. PETROFF. *Arch. mikroskop. Anat.* 97, 54-71(1923).—Rabbits were injected intravenously with carmine in a 2.5% soln. in 4%  $\text{Li}_2\text{CO}_3$  and with colloidal Fe. After repeated Fe injections the deposition of Fe did not take place in all organs which seem to be particularly favorable to the deposition of carmine. The deposition of Fe in amts. capable of detection by microchem. methods takes place primarily in the spleen and liver, with small amts. in the endothelial and reticular cells of the bone marrow and the lymph nodes. The deposition of Fe is not, for the most part, in the same cells which accumulate the carmine. The cells filled with Fe appear to be strongly hypertrophic; the non-hypertrophic cells usually contain carmine and no Fe. The hypertrophy of the Fe-laden cells may be extreme, leading to the formation of multinucleated giant cells filled with Fe and to a lesser degree with carmine particles. Contrary to previously reported work the leucocytes and the lymphocytes did not show an accumulation of Fe. The spleen is the chief organ for the removal of Fe introduced into the circulation. Splenectomized animals, injected with Fe and carmine, showed a slight accumulation of lymphoid elements in the periportal tissue but these cells were devoid of Fe or carmine. The observation that carmine and Fe can be deposited in different cells of the reticulo-endothelial app. warrants the supposition that the cells of this app. (which usually functions as a whole) can in certain cases present a functional differentiation.

G. H. S.

**Rate of deposition and paths of absorption of strontium in the rat.** ETHEL MAY KINNEY AND E. V. MCCOLLUM. *J. Pharmacol.* 21, 165-76(1923).—Sr is deposited in the bones of the body rapidly and in considerable quantity. Its entrance is not inhibited by the presence of Ca in the diet, but it enters the body of a mature rat more slowly than that of a young one. It may enter the body through the placenta, the milk of the mother and the alimentary tract. Sr behaves like Ca in so far as its capability for being deposited in the bones and in the milk is concerned. Sr can in no way replace Ca physiologically as a bone-building element.

C. J. WEST

BRETON, ÉLIANE LE and SCHAEFFER, GEORGES: Variations biochimiques du rapport nucléo-plasmatique au cours du développement embryonnaire. Paris: Masson et Cie. 197 pp. Paper F. 15.

LAZAREV, P.: Physico-chemical Principles of Nerve Activities (in Russian). Moscow: Gosisdat. 62 pp.

## G—PATHOLOGY

H. GIDRON WELLS

**Combined Sachs-Georgi-Wassermann reaction.** EGON KEINING. *Deut. med. Wochschr.* 47, 157-8(1921); *Abstracts Bact.* 5, 474.—A cholesterolized ext. is used as antigen for both the Sachs-Georgi and the Wassermann tests. Other details are not given fully. It is believed that different serum constituents are responsible for these two tests: the Sachs-Georgi being a lipid pptn., and the Wassermann (complement fixation) due to activity of the euglobulins.

H. G.

**A combined Sachs-Georgi-Wassermann reaction.** V. KAFKA. *Deut. med. Wochschr.* 47, 269(1921); *Abstracts Bact.* 5, 474.—A technic similar to that of Keining (cf. above) was employed. After the Sachs-Georgi reaction was completed, complement

and sensitized sheep blood, or first complement and amboceptor followed one hour later by sheep blood were used for the Wassermann. H. G.

**The clinico-diagnostic value of the sugar content of the cerebrospinal fluid.** A. WITTCENSTEIN. *Deut. med. Wochschr.* 49, 246-8(1923).—The sugar content of the cerebrospinal fluid was detd. in a large number of cases, both normal and pathol., the minimetric method of Mandel and Stendel being used. The normal value ranges from 45 to 60 mg. per 100 cc., 50-80% of the blood sugar value. Variations in the blood sugar within normal limits had no effect upon the concn. of sugar in the spinal fluid. An abs. hyperglucemia is associated with an elevation in the sugar content of the spinal fluid. Clinical applications are given. MILTON HANKE

**The urea content of saliva.** MARCELLI LANDSBERG. *Klin. Wochschr.* 2, 306 (1923).—Urea was detd. gasometrically, the NaOBr method being used. Saliva normally contains 18-40 mg. of urea per 100 cc. A urea content above 40 mg. per 100 cc. is suggestive of azotemia. MILTON HANKE

**The relation of the ether- and chloroform-extractable nitrogenous substances of human blood to the blood pressure.** S. J. THANNHAUSER. *Klin. Wochschr.* 2, 388-90(1923).—An Et<sub>2</sub>O ext. prepd. from the blood of patients afflicted with excessive hypertension contains more nitrogenous substance than a similar ext. prepd. from normal blood. The relation N:P obtained in the CHCl<sub>3</sub> ext. also indicates a preponderance of non-lecithin N. There is no parallelism between the Et<sub>2</sub>O-extractable N and the non-protein N. The latter was present in normal amts. in all cases. It has not been possible to elicit a rise in blood pressure in animals with a fractionation product from the blood of hypertonics. MILTON HANKE

**The desensitizing treatment for pollen hypersusceptibility (hay fever).** KARL ESKUCHEN. *Klin. Wochschr.* 2, 407-10(1923).—A detailed discussion of the modern desensitization treatment of hay fever. MILTON HANKE

**Ammonia content of the blood in nephritis.** D. S. RUSSELL. *Biochem. J.* 17, 72-76(1923).—The blood ammonia in 17 cases of advanced renal disease is recorded. The Folin-Denis aeration method, as described by Nash and Benedict (*C. A.* 16, 117), was used. In all cases the values obtained were under 0.1 mg. per 100 cc. and are comparable to the values recorded for eleven cases with no known renal disease. "The evidence available lends support to Nash and Benedict's hypothesis that the kidneys are the site of NH<sub>3</sub> formation in the body, and that the traces found in the systemic circulation represent an overflow from these organs." BENJAMIN HARROW

**Theory of the virus in transmissible lysis of bacteria and the conditions for regeneration of the active principle.** J. BORDET AND M. CIUCA. *Compt. rend. soc. belge biol.* 1922, 33-5; *Physiol. Abstracts* 7, 137(1922).—When it is extremely dil., the principle is regenerated only by the addn. of very small numbers of bacteria. If the bacteria are too numerous, the principle divides its action upon innumerable bacteria, becomes exhausted, and can no longer be regenerated. These facts are not in harmony with the virus theory but support the view that the bacteria reproduce the active principle when they come into contact with it. JOSEPH S. HEPBURN

**Chemical composition of human cerebrospinal fluid.** F. DEPISCH AND M. RICHTER-QUITTNER. *Wiener Arch. inn. Med.* 5, 321-44(1923).—In 167 cases, partly normal and partly pathological, the osmotic concn. of the cerebrospinal fluid was found to be greater than that of the blood serum. The Cl content in general was higher and the Ca and sugar content were lower in the cerebrospinal fluid than in the serum. In a no. of cases no Ca was found in the cerebrospinal fluid and the Ca content of the cerebrospinal fluid seems to be of clinical importance. In 4 cases of severe diabetes, acetone was found in the cerebrospinal fluid and in greater amts. than in the serum. HARRIET F. HOLMES

**Indicanemia an early reliable symptom of insufficiency of the kidney.** GUSTAV BAAR. *Wiener Arch. inn. Med.* 5, 353-7(1923).—Analyses were made of the residual N and indican in the blood and the total N and indican in the urine in 55 cases of kidney disease and 41 cases of other disease. With normal kidney function the indican content of the blood is seldom high, even with a high indican content in the urine. In nephritis high values for indican in the blood were obtained and residual N may be normal in the blood while indican is increased. The detn. of the indican in the blood is a more reliable test for derangement of kidney function than the detn. of the residual N. The indicanemia is not caused by increased formation of indican in the intestinal tract but through retention of indican in the blood, indican being the N-contg. waste product least readily excreted by the kidney. HARRIET F. HOLMES

**The relation of carbon dioxide tension of alveolar air to the secretions of the stomach.** F. KANDERS AND O. PORGES. *Wiener Arch. inn. Med.* 5, 379-408(1923).—A marked

increase of  $\text{CO}_2$  tension in the alveolar air after a test breakfast is shown only in cases with HCl in the gastric secretion. The formation of acid in the stomach, therefore, may be the cause of such an increase in  $\text{CO}_2$  tension, and lack of an increase in  $\text{CO}_2$  tension may indicate lack of acid in the secretion. In carcinoma of the stomach the anacidity is due to a lack of secretion of acid and not to a neutralization of the acid. The low alveolar tension in carcinoma of the stomach seems dependent on the accompanying cachexia.

HARRIET F. HOLMES

**Black water fever.** H. K. BARRENSCHEN AND K. GLAESSNER. *Wiener Arch. inn. Med.* 5, 409-18(1923).—A close relationship of black water fever and malaria is indicated by the agglutination of the erythrocytes of malaria patients by serum from patients with black water fever and the presence of hemolytic substances in the serum of patients with black water fever, bringing about a marked decrease of resistance towards hypotonic NaCl soln. of the erythrocytes of malaria patients, while the erythrocytes of normal individuals show no decrease in resistance.

HARRIET F. HOLMES

**Pituitrin diuresis in nephritis.** O. KLEIN. *Wiener Arch. inn. Med.* 5, 429-50(1923).—Following the injection of pituitrin several types of diuresis were observed. In patients with kidney insufficiency the action of pituitrin is delayed and protracted. Marked differences are shown by edematous and non-edematous patients and pituitrin diuresis may be of clinical importance in indicating the extent of renal and extra-renal lesions.

HARRIET F. HOLMES

**Diabetic edema.** W. FALTA. *Wiener Arch. inn. Med.* 5, 581-90(1923).—In a case of diabetes with marked edema substitution of KCl for NaCl caused a rapid decrease of the edema. With the patient on a diet free from NaCl the administration of  $\text{NaHCO}_3$  was followed by edema which disappeared on the substitution of  $\text{KHCO}_3$  for  $\text{NaHCO}_3$ . After the administration of the bicarbonates the edematous fluid and also the urine showed a low Cl content. The osmotic tension of the edematous fluid was normal and due probably to the increase of carbonates. While most diabetics with edema have acidosis, acidosis cannot be the essential cause of the edema, as edema may occur after the acidosis has disappeared.

HARRIET F. HOLMES

**Action of serum on leukine.** KURT BLUM. *Arch. Hyg.* 91, 373-80(1923).—Leukine is a bactericidal substance present in leucocytes. It is best extd. by digestion with a 5% soln. of inactivated serum in salt soln. In a concn. of 2.5% and greater active and inactive sera inhibit the action of a leukine ext. Smaller concns. either have no action or increase its action. Exudate plasma inhibits the action of leukine.

JULIAN H. LEWIS

**Intracellular oxidation and indophenol blue synthesis.** SIEGFRIED GRÄFF. *Beitr. Path. Anat.* 70, 1-19(1922).—The synthesis of indophenol blue from  $\alpha$ -naphthol and dimethyl-*p*-phenylenediamine by tissues depends on the oxidative capacity of the cells, and is obtained only under certain physiological-chemical conditions. It can be used to differentiate the living cell from the dead and the normal cell from the pathological one. The active agent in the tissues is probably a catalyst which requires a weakly alk. reaction. It is believed that this catalyst is Fe, which explains why HCN inhibits the reaction in low concns. since this substance combines with Fe.

JULIAN H. LEWIS

**Urea content of tissues and the quantitative relation between urea and residual nitrogen in the tissues and blood in normal and pathological conditions.** ERWIN BECHER. *Deut. Arch. klin. Med.* 134, 331-41(1922).—Urea was detd. by the hypobromite method. With the exception of fatty tissue, which contains only a trace, urea occurs in all tissues and the blood in equal amts. in the human cadaver. This is true whether or not there was renal insufficiency. The residual N, however, occurs in the tissues in larger amts. than in the blood. Under normal and pathological conditions urea is a smaller percentage of the residual N in the tissues than in the blood. In renal insufficiency the relation of urea to residual N is changed in both tissues and blood in that larger part (50-77%) of the residual N occurs as urea as compared to the normal figures, 12-20%.

JULIAN H. LEWIS

**Respiratory exchange in disturbances of fat metabolism and diseases of the hypophysis.** RAHEL PLAUT. *Deut. Arch. klin. Med.* 139, 285-305(1922).—With a normal basal metabolism the sp. dynamic action of food can be lowered under 2 conditions, chronic undernourishment and certain disorders of fat metabolism. In undernourishment the reduced rise in metabolism after eating is a purposeful reaction which spares the use of body tissues. If the sp. dynamic action is too low, independent of the state of nutrition, it is due to abnormal fat metabolism and is usually associated with diseases of the hypophysis, especially the symptom complex called dystrophia adiposogenitalis. The theory is advanced that the sp. dynamic action of foods is connected with the

function of the hypophysis either through a hormone secreted by the hypophysis which sensitizes the cells to stimulation by foods or that the hypophysis itself is stimulated by foods to the secretion of a hormone which increases metabolism. It is possible to distinguish thyrogenous-fat diseases from constitutional and hypophyseal fat disturbances. In disturbances of the thyroid in which fat metabolism is affected the basal metabolism is reduced, while in hypophyseal diseases and in habitual leanness it is normal.

JULIAN H. LEWIS

The influence of muscle work on the amount of sugar oxidized in diabetics. E. GRAFE AND H. SOLOMON. *Deut. Arch. klin. Med.* 139, 369-79 (1922).—In all cases of diabetes there was an increase of the amt. of sugar burned (max. increase, 85.6%) as the result of muscular work. The total increase in heat production was more than could be accounted for by the sugar burned. In all cases the amt. of sugar in the urine was decreased, in some cases to 0.

JULIAN H. LEWIS

Immunological significance of vitamins. I. Influence of the lack of vitamins on the production of specific agglutinins, precipitins, hemolysins in the rat, rabbit and pigeon. II. Influence of lack of vitamins on resistance of rat, rabbit and pigeon to bacterial infection. III. Influence of the lack of vitamins on the leucocytes and on phagocytosis. C. H. WAKEMAN. *J. Infectious Diseases* 32, 247-69 (1923).—Rats and rabbits lacking vitamin A or B showed no differences in their ability to produce agglutinins, precipitins, hemolysins or bacteriolysins. Similarly, the pigeon fed a diet of polished rice or a ration lacking vitamin B responded to the injection of antigen with the production of agglutinins. The opsonic index of immunized rats and rabbits showed a depression when there is a deficiency of vitamin A or B in the diet. It is believed that the break in resistance of animals to infection which results from a diet deficient in vitamins is not due to failure to produce opsonins but to the action of a depressive agent on the phagocytic mechanism.

JULIAN H. LEWIS

Study of bacterial products by means of excised mammalian heart. I. Endotoxin of *Spirillum cholerae*. W. H. MANWARING, W. H. BOYD AND S. OKAMT. *J. Infectious Diseases* 32, 307-8 (1923). II. The subhemagglutinin, endotoxin and myotoxin of *Streptococcus hemolyticus*. W. H. MANWARING, W. H. BOYD AND R. C. CHILCOTE. *Ibid* 309-14.—Filtrates from broth cultures of *S. cholerae* are almost non-toxic for the conducting and contractile tissues of the excised rabbit heart. The filtrates, however, are markedly toxic for the capillary endothelium, producing striking myocardial edema and diapedesis. *Streptococcus hemolyticus* grown in 10% defibrinated rabbit blood in Locke's soln. gives products producing the following toxic reactions on the excised rabbit heart: (a) intravascular hemagglutination; (b) marked capillary vasoconstriction; (c) slightly increased capillary permeability; (d) auriculoventricular dissociation (heart-block); (e) marked loss of ventricular tone; and (f) reduction in the strength of ventricular contractions, leading to cessation of recordable movements in from 25 to 30 min.

JULIAN H. LEWIS

Action of lactic acid on experimental infection. JULIUS FREUND. *Z. Hyg.* 97, 363-9 (1923).—A culture of *B. subtilis* contg. lactic acid is fatal when injected into a mouse. The same results occur if the lactic acid is injected simultaneously but separately, showing the action of lactic acid to be that of lowering the resistance of the animal. This action is possessed only by lactic acid and not its Na salt.

JULIAN H. LEWIS

The use of artificial complement in the Wassermann reaction. JULIUS FREUND. *Z. Hyg.* 97, 370-85 (1923).—The artificial complement consists of a mixt. of globulin from beef serum and Na oleinate. This mixt. will complete the hemolysis of red cells with hemolysin. It can be used as a substitute for fresh guinea pig serum in the Wassermann and other complement-fixation tests.

JULIAN H. LEWIS

The antigenic properties of various cold-blooded tubercle bacilli. SELMA MEYER. *Z. Hyg.* 97, 433-49 (1923).—Turtle, snake, frog and "trumpet" bacilli when injected into the human produced sensitization to all the tuberculin of cold-blooded tubercle bacilli but not to that of human and bovine bacilli. When injected into guinea pigs, the frog and snake tubercle bacilli could sensitize only to themselves, while the turtle and trumpet bacilli could sensitize to all the cold-blooded organisms and also to the human bacilli. The Friedmann bacillus is most active of them all. Tuberculous children react not only to tuberculin from warm-blooded bacilli but to the tuberculin of cold-blooded bacilli.

JULIAN H. LEWIS

The "formol gelatinization" of serums and its diagnostic value. L. REINER AND A. MARTON. *Z. Immunitäts.* 36, 133-47 (1923).—The reaction of Gâté and Papacostas is not a sp. reaction for syphilis. It is a coagulation reaction in which formalin has conferred a certain combining capacity upon the albumins, combination and coagulation occurring when particles of such dispersion as globulin, or animal charcoal or lecithin

emulsion are present. Presence of high mol. oxidized protein derivs. makes the serum suitable for formol gelatinization. In general the reaction occurs in those diseases in which other indications of increased protein decompn. are present. E. R. LONG

Studies on conglutination and the variation in the conglutinin content of serum in healthy and diseased cattle. H. M. v. JETTMAR. *Z. Immunitäts.* 36, 148-201 (1923).—In severe, general disease in cattle, febrile or not, the conglutinin content of the serum decreases, without other serum characteristics necessarily being changed. With convalescence the conglutinin content is rapidly restored to normal. As alexin for the conglutinin reaction dog serum has several advantages over human, horse, guinea pig and rabbit serum; among these are stability, absence of hemagglutinating action, marked activity in small amt., and slight individual fluctuation in activity. The most disturbing factor in the reaction is not hemolysis by the alexin, but hemagglutination. The important differences between hemagglutinins and conglutinins are the following: conglutination occurs more rapidly than hemagglutination; in true conglutination the red blood corpuscles adhere in pellicle-like fashion to the walls of the container, while gross clumps settle out in hemagglutination; the clumps formed in true conglutination are more resistant to shaking than the clumps of hemagglutination; shaking of the tube promotes conglutination, while it is without influence or may even hinder hemagglutination. Human, camel, sheep and guinea pig erythrocytes are superior to horse, pig, dog, duck, sparrow, eagle and frog erythrocytes for the indicator in the reaction. Sensitized erythrocytes are the most easily conglutinated; strongly sensitized corpuscles cannot be used, however, as they are easily hemagglutinated. A single freezing and thawing has no influence upon the conglutinin; on long-continued freezing and thawing this constituent concentrates in the lowest liquid layer. Fifteen min. X-raying does not affect conglutinin. Conglutinin is best conserved when serum and clot are removed together. Long standing at 39° destroys conglutinin, but it is not affected by 2 months' standing at room temp. Slight putrefaction affects the conglutinin slightly. Inactivation has a harmful influence. The conglutination reaction may be carried out at low temps. close to 0°. The reaction is best carried out with the following reagents: beef serum in 0.1-0.5 cc. doses, alexinized with dog serum in 10% concn.; 0.5 cc. physiol. NaCl. After 1 hr. 1.0 cc. sensitized sheep erythrocytes and rabbit amboceptor are added. E. R. LONG

Experience with the "serological carcinoma diagnosis." R. WIGAND. *Z. Immunitäts.* 36, 202-14 (1923).—Serum R<sub>2</sub> of an animal treated with human adeno-carcinoma cells gives 86% positive intracutaneous reactions in human adeno-carcinoma. The activity seems to depend upon the simultaneous presence of antigen and antibody. Split products of tumors are not useful for the diagnostic reaction. E. R. LONG

Frequency of the occurrence of heterogenetic precipitin. GERTRUD MEISSNER. *Z. Immunitäts.* 36, 272-287 (1923).—The action of 78 monogenic pptg. antisera, derived from 13 species of animals, was detd. on 12 different animal serum antigens. The number of specific reactions was 55.8%, of heterogenetic, polyergic reactions, 44.2%. In 11.7% of the latter the reaction was as strong with the heterogenetic antigen as with the antigen used in the prepn. of the antiserum. The nourishment and sex of the animal and the season play a role in the development of antisera; with large, old animals in the summer time non-sp. reactions are fewest. E. R. LONG

Anaphylaxis. LXIII. Do relations exist between anaphylatoxin formation in vitro and change in surface tension? E. FRIEDBERGER AND E. PUTTNER. *Z. Immunitäts.* 36, 215-32 (1923).—The surface tension of serums of different animals of the same species is nearly const. On heating serum, surface tension decreases inversely proportionally to the temp. increase, and more rapidly with dild. than undild. serum. It also decreases gradually with age. Surface tension reduced by inactivation of the serum cannot be restored to normal by the addition of fresh serum. Dild. with distd. H<sub>2</sub>O causes a greater increase of surface tension than dild. with an equal amt. of salt soln. or isotonic glucose soln. Kaolin increases surface tension. In the formation of anaphylatoxin from bacteria, as well as the treatment of serum by starch, inulin and agar a significant decrease of surface tension occurs. This occurs equally with active and inactive serums and with suspensions or solns. of starch and inulin. E. R. LONG

Type and nature of isogenetic and heterogenetic precipitation with monogenic antisera. E. FRIEDBERGER AND GERTRUD MEISSNER. *Z. Immunitäts.* 36, 233-71 (1923).—Treatment of an animal of one species with an antigen (monogen) of another species does not produce with absolute regularity an antiserum acting isogenetically upon the injected protein and related protein; such a serum acts upon a whole series of proteins standing close to the injected protein in the phylogenetic scale. Such

condition was found in 47% of pptg. sera, and in 13.5% to the titer limit with the real antigen. Isogenetic ppts. differ morphologically from the heterogenetic. The first are gray, loose and coarsely flocculent, the second white, dense and finely flocculent. The fluid between the particles of the loose ppt. is cloudy; between the fine particles it is clear. The complement-deviation reaction with monogenic-polyergic serums is more sp. than the precipitin reaction. This specificity is less pronounced in the group reactions with related proteins. Isogenetic antigen (unwashed red blood corpuscles) seps. both iso- and heteroprecipitin in satn. procedures. The heterogenetic antigen removes the precipitin for all heterogenetic proteins and only these; in this way serums can be made sp. for practical purposes. Heated antigen (serum), whether it is isogenetic or heterogenetic protein, removes solely all heterogenetic precipitin. E. R. LONG

**Remarks on the publication of A. Wolff-Eisner on experimental contribution to the question of tuberculin-immunity, especially also on the antigenic action of tuberculin.** E. JANUSCHKE. *Z. Immunitäts.* 36, 287-90(1923); cf. C. A. 17, 825. E. R. L.

**Does Moss' grouping of human blood with respect to isoagglutinins apply also to isohemolysins?** SIXTEN HESSER. *Acta Med. Scand.* 57, 415-7(1922).—Reports of examn. of 40 serums which show that human blood can be classified into 4 groups with respect to hemolysis which are similar to the hemoagglutination groupings. S. M.

**Studies of mild glucosurias.** J. E. HOLST. *Acta Med. Scand.* 57, 188-227(1922).—Seventeen cases are described with mild glucosurias which are of benign renal origin and in which functional tests indicate entirely normal conditions either as regards the metabolism or the kidney. S. MORGULIS

**Renal diabetes.** A. JOHNSSON. *Acta Med. Scand.* 56, 485-99(1922).—A record of 2 individuals who for 10 and 16 years, resp., have been eliminating a small amt. of sugar in the daily urine. This was independent of the diet. Their blood sugar was normal, and the blood sugar curve following a test with glucose was normal. S. M.

**Water deprivation of the tissues and the elimination of acetone bodies.** ROBERT EHRSTRÖM. *Acta Med. Scand.* 56, 507-9(1922).—Clinical data are discussed which indicate the possible relationship between excretion of acetone bodies and the withdrawal of fluid from the tissues. S. MORGULIS

**Etiology of the transitory diminution of the refraction in diabetes mellitus.** EMIL ENROTH. *Acta Med. Scand.* 56, 500-6(1922).—Exptl. observations on rabbits and men show that acetone has a tendency to accumulate in the aq. humor in greater concn. than in the blood. In rabbits, either as a result of repeated puncture of the eye ball or through irritation by means of subconjunctival injection of NaCl solns., a very large concn. of acetone may be produced in the eye. It is furthermore assumed that diacetic acid has a similar behavior. The transitory change in the eye refraction leading to hypermetropia in diabetics is attributed to the incident acidosis. The acetone bodies cannot directly affect the refraction, but through osmotic changes an alteration in the lens is established which manifests itself as hypermetropia. S. MORGULIS

**Gold reaction of the cerebrospinal fluid in syphilis of the central nervous system.** G. JANSSON. *Acta Med. Scand.*, Suppl. III, 72-74(1922).—The significance of the colloidal gold reaction is that when it is negative there is no neurosyphilis present. S. MORGULIS

**Alimentary hyperglucemia in arthritis.** OSTEN HOLST. *Acta Med. Scand.*, Suppl. III, 137-8(1922).—In all cases of arthritis examd. there was observed alimentary glucocemia, the max. being reached in 1 hr. and in no instance was the normal level reached again by the end of 2 hrs. Following treatment most of the patients showed practically normal sugar tolerance. S. MORGULIS

**Blood sugar content in anemic conditions, especially in pernicious anemia.** A. JOHNSSON. *Acta Med. Scand.*, Suppl. III, 139-51(1922).—The blood sugar content varies inversely as the no. of erythrocytes or as the hemoglobin % of the anemic blood. Practically in all severe cases the sugar of the blood is increased, but where there are 2.5 million red cells and a hemoglobin of 50-70% the values are generally normal. After feeding 100 g. either as glucose or starch (white bread) the blood sugar curve follows a normal course, though in the more severe cases a greater and more persistent hyperglucemia may result. S. MORGULIS

**Anemia from influenza and the result of iron therapy in such cases.** GUSTAF LINDBERG. *Acta Med. Scand.* 56, 162-87(1922).—The toxic products of the influenza organism injured the bone-marrow in such a manner that anemia of the chlorotic type was caused. Therapy with reduced Fe (as much as 3 g. per day) had a remarkable effect in quickly increasing the blood hemoglobin. S. MORGULIS

**Sugar in pleural and peritoneal effusions.** CH. ACHARD AND J. THIERS. *Compt.*

*rend. soc. biol.* **88**, 252-4(1923).—In febrile cases the sugar level in the fluid is higher than that in non-febrile cases. S. MORGULIS

**Effect of intramuscular injections of magnesium sulfate on the recurrence and metastasis of carcinoma.** RENÉ REDING AND A. P. DUSTIN. *Compt. rend. soc. biol.* **88**, 301-2(1923).—Metastases of breast carcinomas rapidly diminished in vol. after several intramuscular injections of  $MgSO_4$ . There was also evidence of a diminution of the vol. of neoplastic cells. The involution of the metastases results in a general improvement of the condition of the patient. S. MORGULIS

**Is a tyrosinase present in melanotic tumors of the choroid?** J. MAWAS. *Compt. rend. soc. biol.* **88**, 332-3(1923).—The black coloration of tumors of the human eye is not due to the presence of a tyrosinase nor to an oxidation of tyrosine by a peroxidase. S. MORGULIS

**Composition of the hydatid fluid.** P. MAZZOCCO. *Compt. rend. soc. biol.* **88**, 342-3(1923).—The compn. of the fluid from hydatid cysts of man and animals shows certain close relationship to the nonprotein compn. of the blood of the same organism. This is shown by the urea and nonprotein N and NaCl content. The sugar content of the hydatid fluid is considerably less and there is no creatinine in it. S. MORGULIS

**Some physical properties of hydatid fluid.** R. WERNICKE AND E. SAVINO. *Compt. rend. soc. biol.* **88**, 343-4(1923).—Figures are quoted for  $pH$ , viscosity, sp. gr., etc. S. MORGULIS

**The blood calcium of menstruating women and of women at menopause.** THERÈSE MALAMUD AND PIERRE MAZZOCCO. *Compt. rend. soc. biol.* **88**, 396-7(1923).—The av. amt. of Ca per 100 cc. blood was found to be 7.76 mg. in menstruating women and 6.62 mg. in those at menopause, whether natural or temporary (lactation). There is some indication that in cases of precocious menopause the Ca may be increased. S. MORGULIS

**Cerebrospinal fluid of pregnant women.** M. L. PEREZ, S. PUCHULU AND A. J. MORENO. *Compt. rend. soc. biol.* **88**, 398(1923).—The number of cells are normal. There are no variations from the normal either with regard to the amt. of albumin, or Cl, or sugar. In a case of eclampsia an increase in Cl was observed. S. MORGULIS

**Influence of insulin on the blood sugar curve in diabetes.** LEON BLUM AND HENRI SCHWAB. *Compt. rend. soc. biol.* **88**, 463-4(1923).—Corroborative of the findings of American investigators that insulin injection produces a lowering of the blood sugar level, the degree of which depends upon the dose administered, the severity of the case and the time after the injection. The effect of the insulin disappears in about 13 hrs. S. MORGULIS

**Effect of alcoholic extracts of pancreas on the critical glucemia.** H. CHABANIER, M. LEBERT AND C. LOBO-ONELL. *Compt. rend. soc. biol.* **88**, 480-2(1923).—In a diabetic under the treatment with insulin, acetonuria does not appear before the blood sugar level is reduced by 55%, this being also the critical glucemia for the normal person. S. MORGULIS

**Variation in glucemia of a diabetic under the influence of fats.** H. LABBÉ AND B. THEODORESCO. *Compt. rend. soc. biol.* **88**, 483-4(1923); cf. *C. A.* **16**, 4267. —In a diabetic patient with a fixed blood-sugar level the curve following the ingestion of glucose begins to approach the original level sooner by the addition of 50 g. olive oil than without it. S. MORGULIS

**Antihemolytic action of antithrombin.** N. L. COSMOVICI. *Compt. rend. soc. biol.* **88**, 538-40(1923). S. MORGULIS

**Resistance of the red cells in old age and in epilepsy.** L. BALLIF AND MARZA. *Compt. rend. soc. biol.* **88**, 542-3(1923).—In old persons and in epileptics the resistance of the red cell to hemolysis is normal or subnormal. S. MORGULIS

**Anaphylaxis in thymectomized and thyroidectomized animals.** C. J. PARHON AND L. BALLIF. *Compt. rend. soc. biol.* **88**, 544-5(1923).—Extirpation of the thyroid diminishes the anaphylactic shock and saves the animals from death, while the extirpation of the thymus is apparently without any effect. S. MORGULIS

**Prognostic value of high creatinine content of blood in nephritis.** E. JEANNERAU AND P. CRISTOL. *Compt. rend. soc. biol.* **88**, 594-5(1923).—In all cases where the urea retention does not correspond to the gravity of the clinical symptoms the creatinine should be detd. S. MORGULIS

**The ketogenic and antiketogenic balance in the metabolism of Maignon's diabetic dog.** R. CARRASCO-FORMIGUERA. *Compt. rend. soc. biol.* **88**, 611-4(1923).—An examn. of Maignon's data reveals that with a ketogenic-antiketogenic ratio ranging from 3.13 to 4.26 there is a corresponding variation in the acetone excretion. S. M.

**The coefficient of creatinine excretion of the kidney.** P. FONTEYNE AND P. INGEL-

**BRECHT.** *Compt. rend. soc. biol.* **88**, 642-4(1923).—Ambard's formula is applied to the excretion of creatinine. For man this has the value  $0.039 \pm 0.01$ , and is somewhat increased in cases of chronic nephritis. There is no definite relationship between this and the urea coeff., the excretion of the urea generally being subject to much greater variations.

S. MORGULIS

**The carbon dioxide dissociation curve in pulmonary tuberculosis.** LUCIEN DAUTREBAND and H. W. DAVIES. *Compt. rend. soc. biol.* **88**, 647-50(1923).—Tuberculous persons with lesions localized in the apex of the lung have an alk. reserve similar to that of healthy individuals. The blood of patients with a diffuse tuberculous lesion possessed a higher  $\text{CO}_2$ -binding power than that of patients with tuberculosis confined to the apex, and this fact accounts for the circumstance that the blood reaction remains normal in spite of the increased  $\text{CO}_2$  tension in the alveoli.

S. MORGULIS

**Proteolytic and amino acid producing activity of the spleen.** H. DELAUNAY and H. SARROR. *Compt. rend. soc. biol.* **88**, 707-10(1923).—The spleen is remarkably rich in albumoses. The non protein N of the spleen ext. ranges between 180 and 210 mg. with 30-35% of amino acid N and 20% polypeptide N. This indicates that the spleen is the center of active processes of protein cleavage and amino acid production. Owing to the very rapid circulation through the spleen the arterial and venous blood differ almost imperceptibly.

S. MORGULIS

**The retention of albumoses and peptones by the liver.** H. DELAUNAY and J. DESQUEYROUX. *Compt. rend. soc. biol.* **88**, 710-2(1923).—The introduction of large quantities of peptone (1-1.2 g. N) into an isolated loop of the intestine is not followed by albumosuria although the material is almost completely absorbed. On the other hand, the injection into the portal system of very small amts. of peptone (10-20 mg. N) produces a strong albumosuria. The same effect can be obtained by injections into the general circulation. The expts. indicate that only the small intestine can hold back and transform albumoses and peptones during digestion. The liver in this respect is not unlike all other organs.

S. MORGULIS

**Calcium and magnesium in the serum of normal persons and of patients with hypertension or atherosclerosis.** M.-P. WEIL, CH. O. GUILLAUMIN and R. WEISMANN-NERTER. *Compt. rend. soc. biol.* **88**, 732-4(1923).—In individuals with a normal  $p_{\text{H}}$  (7.5) and bicarbonate reserve (65 vol.  $\text{CO}_2$ ) the serum contains 100-120 mg. Ca and 15-20 mg. Mg per 100 cc. The  $\text{Ca/Mg} = 6.36$ . In nephritic individuals with hypertension the Ca is within the same limits, but the  $\text{Ca/Mg}$  is generally less than normally. In atheromatous patients, on the other hand, with or without hypertension there is frequently a great increase in the serum Ca but the  $\text{Ca/Mg}$  ratio remains within normal limits even in very advanced conditions.

S. MORGULIS

**Hypercalcemia in chronic rheumatism.** MATHIEU-PIERRE WEIL and CH. O. GUILLAUMIN. *Compt. rend. soc. biol.* **88**, 734-5(1923).—The Ca in the serum of rheumatic individuals is usually greatly increased; only in the case of the milder conditions is this not invariably found. The Mg and the combined uric acid show likewise an increase.

S. MORGULIS

**Basal metabolism of incipient tuberculosis.** V. CORDIER. *Compt. rend. soc. biol.* **88**, 782-4(1923).—An increased basal metabolism in incipient cases of tuberculosis is an unfavorable prognostic sign; this is in the majority of instances associated with a condition of hyperthyroidism.

S. MORGULIS

**Influence of adrenal glands on diabetic hyperglucemia.** DAVID BOEGGILD. *Compt. rend. soc. biol.* **88**, 816-8(1923).—Cauterization of the medullary substance of the adrenal glands of dogs prevents the usual high hyperglucemia resulting from the ablation of the pancreas. It is possible that an excess of adrenaline affects the pancreatic hormone in such a way as to result in a rise of the blood sugar level.

S. MORGULIS

**Determination of cholesterol in therapeutic serums.** A. MARIE. *Compt. rend. soc. biol.* **88**, 875-7(1923); cf. *C. A.* **17**, 1839.—The cholesterol level of antidiphtheric and antitetanic serum from horses is appreciably above or below the cholesterol titer of normal serum. But in most instances the cholesterol level varies inversely with the number of antitoxic units.

S. MORGULIS

**Functional value of external pancreatic secretion in conditions of hyperchlorhydria.** M. GAROFANO. *Compt. rend. soc. biol.* **88**, 945-7(1923).—The amts. of amylolytic and tryptic enzyme are increased in conditions of hyperchlorhydria, this increase being the more pronounced the weaker the hyperchlorhydria. Excessive chlorhydria may destroy the enzymes and thus secondarily disturb the intestinal digestive process.

S. MORGULIS

**Hemoclastic shock.** L. HANNAERT. *Compt. rend. soc. biol.* **88**, 981-2(1923).—The mesenteric blood has a considerably higher amino acid N content than the systemic



blood. Autoclaving does not affect the total amino acid N of either, thus showing that these bloods, unlike the portal circulation, contain no polypeptides. S. MORGULIS

**Normal and pathological amino-aciduria.** CHARLES RAHIER AND MAURICE REGNIER. *Compt. rend. soc. biol.* **88**, 983-5(1923).—A study of the amino acid N in urines both from normal and pathological individuals fails to reveal any difference in the concn. which may be attributed to the affection. S. MORGULIS

**Changes in  $p_H$  of the plasma at the time of anaphylactic shock and its relation to lowering of surface tension.** EDGARD ZUNZ AND JEAN LA BARRE. *Compt. rend. soc. biol.* **88**, 990-1(1923).—The  $p_H$  of the plasma diminishes during anaphylactic shock. The alkalinity tends to diminish the more the severer the symptoms are, and the plasma may even become slightly acid. The surface tension likewise falls. S. MORGULIS

**Data concerning autolysis of elastic tissue.** Y. TRITCHKOWITCH. *Compt. rend. soc. biol.* **87**, 1135-6(1922).—There is no evidence of autolysis. S. MORGULIS

**Studies on the calcification of the callus.** E. P. LEHMAN. *Arch. Surg.* **6**, 784-92 (1923).—Exposure to sunlight and the addition of cod-liver oil to the diet exert no measurable accelerating influence on the calcification of fracture callus in normal rats. JOHN T. MYERS

**Influence of temperature on antigens and antibodies.** THORWALD MADSEN. *J. State Med.* **31**, 151-76(1923).—A summary is given of the work of 20 years on the interrelations of toxin and antitoxin at the State Serum Institute, Copenhagen. The scheme was (1) to study the laws of the actions of a no. of antigens on their medium, (2) to exam. the laws of the destruction of antigens and antibodies and further in both cases to study the influence of H-ion concn. and of temp. on these processes. The actions of trypsin and of pepsin on thymol-gelatin and of trypsin on casein proceed according to the formula for bimolecular reactions  $dq/dt = K(a - q)^2$ , the observed and calcd. results closely agreeing. The relation between the rate of reaction of trypsin or pepsin and temp. follows closely the formula enunciated by van't Hoff and Arrhenius. These laws hold good for the coagulating action of the fibrin enzyme on plasma, the tryptic action of pyocyanus cultures on thymol-gelatin, for the rennet enzyme and for the action of trypsin on coli-agglutinin. The influence of H-ion concn. and of enzymic concn. were studied. The deterioration of trypsin, pepsin and rennin by heat follows the monomolecular reaction formula  $dq/dt = K(a - q)$ . The destruction of vibriolysin at 45.97° and at temps. ranging from 45.145 to 49.975° follows closely the monomolecular formula. Analogous results were found with other toxins, such as tetanolysin, streptolysin, epeiralisin and epeiratoxin (cross-spider poison). The destruction of diphtheria toxin was bimolecular. The course of reaction of the complement is monomolecular, and the relation between the rate of reaction and the temp. follows the usual temp. law, though other factors play a part in the deterioration of complement at low and at high temps. Agglutinins when destroyed by heat show rather intricate relations as some follow the law of monomolecular reactions, others the bimolecular. Both immune and normal amboceptors usually decompose at temps from 60° to 70°, following as a rule the monomolecular reaction law. The destruction of diphtheria antitoxin does not occur until such a high temp. is reached that the serum is coagulated by the heat; it should therefore be dild. 1 to 3. This reaction is bimolecular. The rapid deterioration of diphtheria antitoxin at high temps. and its decrease in potency at room or ice-box temps. can be expressed by the bimolecular formula. Neither the alteration in viscosity nor coagulation of the serum followed the same laws as those applicable to the destruction of the antitoxin. Hemolysis by vibriolysin on horse blood at varying temps. when represented by graphs in which the percent of undissolved corpuscles is plotted against time is comparable to an ordinary chem. process. The processes of agglutination, disinfection, and phagocytosis conform to the same laws. Since the various reactions studied conform to simple chem. laws and the influence of temp. in these reactions follows laws applicable to chem. phenomena, it is to be expected that ultimately immuno-chemistry will be brought into the ranks of the exact sciences. J. W. RIGGS

**Tetany in the adult, with special reference to alkalosis and calcium metabolism.** WILDER TILSTON AND F. P. UNDERHILL. *Am. J. Med. Sci.* **165**, 625-36(1923).—In 3 cases of tetany the bicarbonate of the blood was increased. In 1 a low serum Ca was noted and the Ca metabolism was abnormal. Fat absorption was poor although the N balance was positive. The urine showed a high ammonia N although no other signs of acidosis were noted. The indican of the urine was increased. G. H. S.

**Significance of physical chemistry in surgery.** H. SCHADE. *Arch. klin. Chir.* **123**, 784-95(1923).—A discussion of the relation of the action of ions and of colloidal systems and physico-chem. phenomena to such processes as wound healing, suppuration, hyperemia, edema, the formation and resolution of adhesions, the formation of gall-

stones, the resistance of bones to fracture, disinfection, local anesthesia, and narcosis.

G. H. S.

**Erythrocyte sedimentation.** JOSEF VORSCHÜTZ. *Med. Klin.* 19, 269-72(1923).—The sedimentation of erythrocytes involves an electrochem. process in which the positively charged globulins of the serum and the negatively charged red blood cells take part. The non-specific Widal reaction depends upon the same phenomenon and sera which give a non-specific agglutination of bacteria also show alteration of the sedimentation rate of erythrocytes. The disturbed reactions noted in pregnancy, carcinoma, tuberculosis, and in other infections are referable to a globulin increase of the serum, as related to its albumin content. Variability in the charge of the cells is important and is associated with variations in the protein content. G. H. S.

**Significance of uric acid in diffuse nephritis.** AUFRICHT. *Med. Klin.* 19, 340-1 (1923).—In all types of diffuse nephritis the disturbance is to be referred directly, or indirectly, to the action of uric acid. G. H. S.

**Colloid color reactions in the cerebrospinal fluid.** PAUL KIRCHBERG. *Med. Klin.* 19, 387-8(1923).—The Berlin blue reaction with spinal fluid is of diagnostic value in neurosyphilis only when it takes place within 5 to 20 min. after the addn. of the dye to the fluid dilns. The amt. of ppt. formed is proportional to the severity of the involvement. The indigo reaction is positive if a ppt. can be observed within 20 min. to 1 hr. after mixt. of the fluids. G. H. S.

**Alimentary leucocytosis in its relation to the "crise hémoclasique" of Widal.** W. STORM VAN LEEUWEN, Z. BEIN AND H. VAREKAMP. *J. Exptl. Med.* 36, 415-26 (1922).—Counts of white blood cells at short intervals after the ingestion of a meal do not give evidence of the existence of a *crise hémoclasique* and consequently cannot be used to identify the causative agent of cases of hypersensitiveness to foodstuffs or drugs. Whether such an identification can be obtained if, instead of simply counting white cells, the whole complex of symptoms originally described by Widal as characteristic for a *crise* is used, remains undetd. by this work. C. J. WESS.

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## H—PHARMACOLOGY

ALFRED N. RICHARDS

**The vascular and diuretic action of small doses of digitalin on the rabbit.** L. BECO AND L. L. PLUMIER. *J. physiol. path. gén.* 20, 346-55(1922).—Intravenous injection of small doses of strophanthin, digitalin, or digitalein produces a diminution of diuresis in the rabbit. In a rabbit on the operating table, especially when narcotized, there results glucosuria in consequence of intravenous injections, or even previously to any injection. This glucosuria increases during an expt. and is accompanied by a distinct polyuria. The latter accounts for statements that digitalin has diuretic properties when injected in small doses into healthy animals. A. T. CAMERON

**Krysolgan treatment of pulmonary tuberculosis.** F. L. WEIG. *Beitr. klin. Tuberk.* 51, 211-22(1922).—The best indicator of a Krysolgan reaction is the pulse frequency. The Krysolgan diverse action is explained as an increased tissue reaction and metabolism or a toxin-destroying action. Natural healing is hastened. Phys.-chem. considerations are drawn upon to explain further the Krysolgan action. Parallel with the acuity of the inflammatory reactions there is an ion shifting and the osmotic relations in the lesions are changed. In chronic tuberculous lesions equalization of reactions is nearly complete. After exertion, cooling, tuberculin and Krysolgan treatment a shifting occurs resulting in a focal reaction. If the regulation is complete Krysolgan action is absent. Deficient circulation of fibrous foci is a partial basis for the absence of Krysolgan action. In the focal reaction the colloid chem. changes of the vascular walls play a part. In fibroid cases the focal reaction may not be determinable but with prolonged treatment a therapeutic effect can attain. The increased cell de-

struction is to be attributed to fermentative, besides hyperosmotic and hyperacidotic, processes. The increased scar tissue formation appears especially after marked reactions. In successful cases the exudative symptoms can markedly increase. Lymph-stasis is significant in Krysolgan action. Increased cellular elements occur in the sputum and there is a change in the blood picture increase in the polynuclears and shift of the leucocytes to the left (Arneht). Platelets decrease temporarily; immune substances are made mobile and old Deycke-Much papules flare up again. Krysolgan was successfully used with Much's MTb R, partigens and albumose-free tuberculin. Evident tuberculin tolerance occurred during Krysolgan treatment. As concomitant actions were found gastrointestinal disturbances, hyperacidity and hypergastric secretion.

H. J. CORPER

The action of chloroform, ether and xylene extracts of tubercle bacilli and Phymatin ointment upon the conjunctiva of tuberculous and healthy cattle. ERNST FINDERLIN. *Beitr. klin. Tuberk.* 51, 236-51 (1922).—Phymatin causes a mucopurulent exudate in the conjunctiva of tuberculous cattle which persists as a lachrymation after 24 hrs. or as a marked conjunctivitis with reddening and swelling of the mucous membranes and lid. The liquid "Phymatin" was in every way replaced by the 80% Phymatin ointment. Whole bacilli contain substances which act upon the conjunctiva of tuberculous cattle specifically like Phymatin. Bacilli freed from the xylene, ether and  $\text{CHCl}_3$  ext. retain the sp. irritating substance similar to Phymatin. The conjunctiva of tuberculous cattle do not react to the xylene, ether and  $\text{CHCl}_3$  sol. substance of the tubercle bacillus. Therefore allergically determinable fat antibodies in the sense of Much are not demonstrable.

H. J. CORPER

Experimental studies on the arsphenamine therapy of general paralysis. R. WEICHBRODT. *Deut. med. Wochschr.* 47, 69-71 (1921); *Abstracts Bact.* 5, 487.—After intravenous injection of arsphenamine preps. As is to be found in the blood and the spinal fluid in a very short time. The amt. of As is about equal in both fluids. As is also to be found in the brains of those receiving treatment with arsphenamine. It is believed that comparative tests on animal brains should det. the value of new As preps.

H. G.

The toxicity of tobacco smoke, particularly cigaret smoke. R. HEINZ. *Deut. med. Wochschr.* 49, 318-9 (1923).—Chewing tobacco contains very little nicotine. Pipe tobacco contains less than cigar tobacco. The latter frequently has a nicotine content of 7%. Cigar smoke varies greatly in nicotine content. Smoke from a moist cigar contains 50-75% more nicotine than smoke from a dry cigar. Seven cigarets (combined wt. 5 g.) contained 0.25 g. nicotine. The smoke from them contained 0.04 g. nicotine, of which 0.007 g. was absorbed by the mouth smoker and 0.035 g. by the inhaler. Nicotine was detd. pharmacologically. App. and methods are described in detail.

MILTON HANKE

The reaction energy of organic arsenic and antimony compounds with special reference to their biological action. HANS SCHMIDT. *Klin. Wochschr.* 2, 352 (1923).—The quinivalent Sb and As compds. were treated with an excess of  $\text{SO}_2$  for a definite period of time. The  $\text{SO}_2$  was then removed and the amt. of unchanged quinivalent As and Sb detd. titrimetrically.  $\text{K}_3\text{H}_7\text{Sb}_2\text{O}_7$  was reduced to the extent of 11%; but under the same conditions  $\text{PhSbO}(\text{OH})_2$  and  $p\text{-AcNHC}_6\text{H}_4\text{SbO}(\text{OH})_2$  were reduced to the extent of 80 and 70%, resp. Obviously, then, the quinivalent Sb compds. in which Sb is combined with C are more easily reduced than the inorg. Sb compds. The trivalent forms of As and Sb are the therapeutically active forms. Org. quinivalent Sb and As compds. are more effective, therapeutically, than the inorg. derivs., because the former are more easily reduced. The direct injection of org. trivalent derivs. is apt to give rise to severe local reactions; hence the advisability of using the less irritating quinivalent derivs.

MILTON HANKE

The action of the potassium ion on electrical irritability. E. FRANK, M. NOTHMANN AND A. WAGNER. *Klin. Wochschr.* 2, 405-6 (1923).—Elec. irritability was detd. in the case of a normal adult after the ingestion of 20-30 g. of each of the following salts:  $\text{K}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{KCl}$ ,  $\text{KHCO}_3$ ,  $\text{KOAc}$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{NaCl}$ ,  $\text{NaHCO}_3$ ,  $\text{NaOAc}$ . The elec. irritability is increased markedly by the K ion and by the alk. reacting anions. Of the latter the  $\text{HPO}_4$  ion is the most effective; but  $\text{OAc}$  and  $\text{HCO}_3$  are also effective. Na seems to have no action;  $\text{NaCl}$  is ineffective. An acid reacting anion ( $\text{H}_2\text{PO}_4$ ) reduces the effectiveness of the K ion.  $\text{NH}_4$  ion and especially  $\text{NH}_4\text{H}_2\text{PO}_4$  reduce the elec. irritability.

MILTON HANKE

The action of the phosphate ion on electrical irritability. E. FRANK, M. NOTHMANN AND A. WAGNER. *Klin. Wochschr.* 2, 406 (1923).—A mixt. of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ , pH 7.0, fed to healthy adults increases the elec. irritability for from 5 to 10

min.  $\text{Na}_2\text{HPO}_4$  gives a similar though more lasting effect (30–40 min.). Cf. preceding abstr.

MILTON HANKE

**Production of momentary cardiac arrest by ammonium chloride. Its analogy to inhibition of pneumogastric origin.** H. BUSQUET. *Compt. rend. soc. biol.* 86, 106–7 (1922).—When an isolated rabbit heart is perfused with a nutritive soln. free from K, then with a similar soln. containing  $\text{NH}_4\text{Cl}$ , an arrest of the heart beat closely resembling vagus inhibition occurs at the moment of change from the first to the second soln. This phenomenon occurs even when the vagus terminations are paralyzed. This effect of  $\text{NH}_4\text{Cl}$  is presented as evidence that the normal vagus effect is not due to liberation of K ions.

JOSEPH S. HEPBURN

**Coccus indicus; a review of the verification of its symptomatology.** LANN J. BOYD. *J. Am. Inst. Homeopathy* 15, 891–7 (1923).—A critical review, with elaborate bibliography, of the physiol. action of fish berries.

JOSEPH S. HEPBURN

**Pharmacological action on blood sugar.** M. GROSSMANN AND J. SANDOR. *Wiener Arch. inn. Med.* 5, 419–28 (1923).—Adrenaline, atropine and pilocarpine were injected in the same patients on 3 successive days and detns. of the blood sugar were made at frequent intervals. Adrenaline usually caused an increase in blood sugar, particularly marked in two patients with Basedow's disease. Atropine did not affect the blood sugar content of the Basedow patients but caused a slight decrease in blood sugar in normal persons and a marked but transitory decrease in two cases of diabetes. The cases of diabetes not reacting to atropine showed only a slight reaction to adrenaline. Pilocarpine seemed inconstant in its action.

HARRIET F. HOLMES

**Pharmacology of the vegetative nervous system.** R. HOFFMANN. *Wiener Arch. inn. Med.* 5, 543–52 (1923).—The action was studied of various adrenaline-pilocarpine combinations on the secretion of sweat, saliva and sugar. The effect depends chiefly on the condition of the autonomic nervous system produced by the drug used first. The glucosuric action of adrenaline is increased if followed by an injection of pilocarpine but is inhibited if preceded by the pilocarpine injection.

HARRIET F. HOLMES

**The treatment of anemias with colloidal metals.** BERTA ASCHNER. *Wiener Arch. inn. Med.* 5, 523–42 (1923).—From its colloidal nature electroferrol seemed to be theoretically the Fe prepn. most suited for the treatment of anemias. Increased stimulation of the blood-forming organs and decreased activity of the reticulo-endothelial system through deposition of Fe in the cells was expected. Electroferrol, however, was found to have no effect on 9 cases of anemia of different origin. In a case of pernicious anemia treated with electroferrol and injected shortly ante mortem with colloidal Ag, the reticulo-endothelial system showed only traces of Ag and there was no indication of increased Fe retention.

HARRIET F. HOLMES

**Blood changes produced by inhaling lead dust.** HANS RAUCH AND L. MICHAELIS. *Arch. Hyg.* 91, 293–300 (1922).—Rabbits were exposed to Pb dust and the time of onset and nature of the blood changes induced. The early appearance of nucleated basophilic granular and polychromatic red cells lead to the suggestion that the diagnosis of early Pb poisoning should be made from blood exams.

JULIAN H. LEWIS

**Inhalation of lead dust.** E. NEHRING. *Arch. Hyg.* 91, 301–14 (1923).—Unsuccessful expts. were made with cats to learn if Pb poisoning occurs by absorption of Pb through the lungs or through the mucous membrane of the nose, mouth and gastrointestinal tract.

JULIAN H. LEWIS

**The extermination of nits by means of antiformin.** A. V. JENNY. *Centr. Bakt. Parasitenk., I Abt.* 89, 292–3 (1923).—Antiformin dissolves the chitinous capsule of nits. It is used in an 8–10% soln. to loosen nits in the hair.

JULIAN H. LEWIS

**Action of arspenamine in experimental staphylococcus infection in rabbits.** SHIN MATS. *Z. Hyg.* 97, 99–115 (1923).—Rabbits given arspenamine simultaneously with an infective dose of staphylococci died sooner than those given staphylococci alone because of the marked organotropic action of arspenamine.

JULIAN H. LEWIS

**Chemotherapy with 3,6-diaminoacridine compounds and other dyes.** O. SCHIRMANN. *Z. Hyg.* 97, 280–310 (1922).—Several compds. of the acridine series, triphenylmethane derivs. and quinoline derivs. were found to be active against septicemic bacteria. With all these substances is observed Ehrlich's *effectus contrarius* in which subtherapeutic doses lead to a stimulation of the infection. In most expts. subcutaneous or intraperitoneal treatment 5–15 mins. after infection was effective. In some instances results were positive 2–4 hrs. after infection. Several expts. with intravenous treatment were negative even with repeated injections. It is better to administer it subcutaneously or intraperitoneally in oily soln. With streptococci and Friedländer bacilli positive results are obtained only by intraperitoneal treatment. This is a question of local action. Among the acridine compds. there is no optimal substance that

can be used for general treatment on account of a marked organotropic action. The acridine compds. are the only chem. substances with which cholera can be cured. Trypaflavine disappears relatively fast from the circulation of the mouse. Expts. with the effect of these compds. on septicemias in other animals than the mouse were negative (g. inea pigs, rabbits and chickens). Quinoline yellow is markedly inhibitive *in vitro* and bactericidal *in vivo*. A strain of streptococcus which was not influenced by optochin was killed by trypaflavine *in vitro* and *in vivo* the same relations held. HgCl<sub>2</sub> had a curative action in Freidländer bacillus infection. Its action was purely local. Dilns. of these substances which no longer inhibited growth lower the virulence of the organisms. Bactericidal action, inhibition of development and lowering of resistance are part of the same phenomenon but the nonsp. increase of the resistance of the test animal is entirely different. The chief interest in these compds. is their use as stepping stones to the development of more active substances.

JULIAN H. LEWIS

The treatment of sleeping sickness by atoxyl and its regulation. OUZILBAU AND LÉPROU. *Ann. inst. Pasteur* 37, 275-93(1923).—Atoxyl is the best medicament for sleeping sickness. Refutation is presented for several arguments against its use.

E. R. LONG

Treatment of sleeping sickness in the second stage. LÉPROU. *Ann. inst. Pasteur* 37, 294-321(1923).—Arsenicals have not proved very effective. Prophylactic and symptomatic treatment should be employed, with an occasional injection of atoxyl to keep the peripheral circulation sterile.

E. R. LONG

Safety of local anesthetics, with particular reference to cocaine and butyn. CARL NIELSEN AND J. A. HIGGINS. *J. Lab. Clin. Med.* 8, 440-53(1923).—The min. fatal dose of butyn injected subcutaneously in rabbits and dogs is 55 mg. per kg. body wt. That of cocaine is 45 mg. The higher the development of the brain in an animal, the higher is the toxicity of cocaine. Of various drugs investigated for their detoxicating action in poisoning by local anesthetics of the so-called cocaine group pituitary soln. appeared to be the best. Small subcutaneous injections of pituitary ext. simultaneously with the local anesthetic prevented the fall in blood pressure from therapeutic doses, the convulsions from higher doses, and death from lethal doses. Used as an antidote where convulsions had already set in it was effective if injected intravenously. Its use is naturally contraindicated in pregnancy and high blood pressure.

E. R. LONG

The toxicity of arsenobenzene. G. CASTELL. *Z. Immunitäts.* 36, 97-121(1923).—Of the various factors influencing the toxicity of arsenobenzene oxidation is of great clinical importance. Expts. with the organism of relapsing fever indicated that solns. of arsenobenzene allowed to stand in the air 1-2 hrs. after prepn. became slightly more toxic for the parasite and considerably more toxic for the exptl. host.

E. R. LONG

Pharmacological essay of a heart-stimulating glucoside extracted from *Thevetia nerifolia*. RENÉ WRITZ AND ANDRÉ BOULAY. *Compt. rend. soc. biol.* 87, 1105-7(1922).—This is an amorphous levorotatory glucoside which is slightly sol. in H<sub>2</sub>O and melts at 191°. Half a mg. injected into a guinea pig has no visible effect, but 2 mg. given subcutaneously to a 0.5-kg. animal brings about loss of oculopupillary reflex, respiratory arrest and death in less than 30 min. The auricles and ventricles, however, continue beating for about 1/2 hr. In dogs under chloral 0.25 mg. injected intravenously produces a temporary rise of the carotid pressure, and with 2 mg. the rise in pressure reaches 3-6 cm. and the kidney vol. diminishes. The heart remains normal and the vagus excitable, but on repeating the injection 20 min. later arrhythmia and vagus paralysis are produced, which lead rapidly to death. The glucoside behaves somewhat like ouabaine.

S. MORGULIS

The presence of a powerful vasoconstrictor principle in *Genista*. H. BRUGUET AND CH. VISCHNIAC. *Compt. rend. soc. biol.* 87, 1116-8(1922).—Extracts obtained by a certain treatment (the plants at flowering time are dried in a current of warm air; the stalks are then macerated, extd. with CHCl<sub>3</sub> and ether, and pulverized; this powdered material is now extd. with H<sub>2</sub>O in a Soxhlet app. and the ext. concd. in a partial vacuum) have a vasoconstricting power greater than that of adrenaline or ergot. The substance acts directly on the vascular musculature without the intervention of the nervous system.

S. MORGULIS

Action of different metals on tumor grafts of the rat through ionotherapy. A. BORREL, A. DE COULON AND L. BOEZ. *Compt. rend. soc. biol.* 87, 1118-21(1922).—A current of definite amperage was passed through rats with tumor grafts of different duration of growth in such a way that the carbon anode rested on a wad of cotton soaked in a series of different salts and applied directly over the tumor. NaCl, KCl, CaCl<sub>2</sub>, FeSO<sub>4</sub>, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, and Na<sub>2</sub>SeO<sub>3</sub> all gave entirely negative results. With BaCl<sub>2</sub>, CuSO<sub>4</sub>, and AgNO<sub>3</sub> a few of the rats treated were cured. But the most striking results were

obtained in the treatment with  $Pb(NO_3)_2$ , where 8 out of the 10 rats subjected to the electrical treatment were cured.

S. MORGULIS

The action of large doses of physostigmine sulfate on the enucleated eye of the frog. Cf. GAUTIER. *Compt. rend. soc. biol.* 87, 1129-30(1922).—A 1-2% soln. of physostigmine sulfate causes dilatation of the pupil though not in so marked a degree as adrenaline. Cf. C. A. 17, 1672.

S. MORGULIS

Effect on the blood of the diglucoside of dihydroxydiaminoarsenobenzene. A. LUQUET. *Compt. rend. soc. biol.* 87, 1163-5(1922); cf. C. A. 17, 1081.—This compd. is said to have a less marked influence within the therapeutic doses on the blood elements than arsphenamine: its administration does not produce a very great fall in the no. of red cells and does not bring about the alteration in the differential leucocyte count.

S. MORGULIS

Pharmacodynamic properties of the hydatid fluid. L. GIUSTI and E. HUG. *Compt. rend. soc. biol.* 88, 344-6(1923).—Intravenous injections into dogs causes symptoms of shock. There is rapid fall of blood pressure, rapid pulse, leucopenia and diminished coagulability of the blood. Atropinization does not prevent the onset of shock, but this may be delayed by adrenaline or  $BaCl_2$ . This action is not apparently due to histamine because it has no broncho-constrictor effect. In a diln. of 1:10000 it produces a strong contraction of the virgin guinea pig uterus; 1:1000 diln. causes contraction of the isolated intestine. Adrenaline is antagonistic.

S. MORGULIS

Effect of snake venoms on the medullary centers. G. PACILLA. *Compt. rend. soc. biol.* 88, 366-7(1923).—Injections of dry venoms from a variety of snakes show the following effects: there is a quick and persistent hypertension occasionally preceded by a very brief hypotension; frequently bradycardia occurs; respiration is affected a little later becoming slow and of the Cheyne-Stoke type before complete arrest. There are no motor symptoms except in the case of the venom from *Crotallus terrificus*.

S. MORGULIS

The mechanism of curarization caused by snake venoms. B. A. HOUSSAY and J. GUGLIELMETTI. *Compt. rend. soc. biol.* 88, 367-8(1923).—This effect is due to the direct action of the venoms on the muscles.

S. MORGULIS

Effect of snake venoms on thrombin and antithrombin. ROSE RABINOVITCH. *Compt. rend. soc. biol.* 88, 369-70(1923).—Cobra venom is without any effect on hirudin. It destroys vigorously the antithrombin action of peptone plasma and prevents the formation of Howell's antithrombin. It makes the blood incoagulable but not anticoagulant.

S. MORGULIS

Hemorrhagic pancreatitis caused by snake venoms. C. PREIONI. *Compt. rend. soc. biol.* 88, 370-1(1923).—The venom activates the digestive enzymes intrapancreatically and this leads to a dissolution of its tissue with hemorrhage.

S. MORGULIS

Pharmacodynamic action of toad venom. V. NOVARO. *Compt. rend. soc. biol.* 88, 371-3(1923).—Dilns. 1:5000 up to 1:200000 cause strong contraction of an intestinal segment, and the venom is therefore antagonistic to adrenaline. It dilates the pupil of the enucleated frog eye. Subcutaneous injection of 0.05 g. restores the contracting power of the fatigued frog gastrocnemius; it inhibits pancreatic secretion but may cause a slight response of the salivary glands. When injected subcutaneously into a 2-kg. rabbit 0.3 g. of the venom suffices to produce a strong glucosuria. S. M.

Diuretic action of bismuth; mechanism of this action. LÉON BLUM. *Compt. rend. soc. biol.* 88, 461-3(1923).—Bi causes considerable diuresis with large elimination of NaCl. The diuretic effect is due not to the latter circumstance, but to a direct stimulation of the renal cells as in the case of Hg.

S. MORGULIS

The physiological action of ergotamine, the active principle of rye ergot. E. ROTHLIN. *Compt. rend. soc. biol.* 88, 470-2(1923).—In its action on the uterus and on the cardiovascular system ergotamine shows the same characteristics as rye ergot, and by virtue of its purity and well defined chemical nature gives greater assurance of constancy than other preps.

S. MORGULIS

Hypertoxicity of neoarsphenamine for rabbits prepared by subcutaneous injections of sheep serum. A. THIBOUX, C. BOUVELOT and J. ARILO. *Compt. rend. soc. biol.* 88, 491-3(1923).—Sheep serum is toxic if given to rabbits intravenously. When given subcutaneously it does not injure the health of the rabbits; they gain weight but become more sensitive to toxic products such as neoarsphenamine.

S. MORGULIS

Effect of adrenaline on the thymus. JACQUES GOLDNER. *Compt. rend. soc. biol.* 88, 545-8(1923).—New-born puppies were given daily for 30 days an injection of  $\frac{1}{2}$  cc. of a 1:1000 adrenaline soln. An examn. of the thymus glands shows that this organ has been greatly stimulated in the processes of its evolution and involution. This

effect is not a sp. result of the excess of adrenaline but is also produced by X-ray treatment or by starvation. S. MORGULIS

**Scorpion poisoning and the adrenaline-chloroform syncope.** E. BARDIER AND A. STILLMUNKES. *Compt. rend. soc. biol.* 88, 559-61(1923).—The venom of the Algerian scorpion has a cardiovascular action similar to that of adrenaline but it does not cause the fatal syncope under the influence of chloroform anesthesia. S. MORGULIS

**Effect of adrenaline and suprarenal extracts on the excitability of muscles.** ALBERT OBRÉ. *Compt. rend. soc. biol.* 88, 585-8(1923).—Adrenaline has no favorable action on muscular excitability. Suprarenal gland ext., on the contrary, increases the excitability. Adrenaline, therefore, is without its usual physiological action as far as striated muscle fibers are concerned. S. MORGULIS

**The in vivo adsorption of the salicylate ion by blood serum.** The mode of secretion of the salicylate ion by the kidney. H. CHABANIER, M. LEBERT AND C. LOBO-ONELL. *Compt. rend. soc. biol.* 88, 608-10(1923).—Expts. are discussed which seem to show that salicylate is adsorbed by the blood proteins and that its elimination is independent of any renal threshold. Cf. C. A. 17, 1808. S. MORGULIS

**Action of urates in augmenting the excitability of inhibitory and diminishing that of the accelerating heart nerves.** HENRI FREDERICQ AND ALBERT RADELLET. *Compt. rend. soc. biol.* 88, 623-5(1923).—Intravenous injections of a neutral soln. of K urate increase the excitability of the fibers of the vagus, and diminish or entirely abolish the cardiac effects of the stimulation of the accelerating fibers from the ansa of Vieussens. S. MORGULIS

**Amino acids are without influence upon the glucolysis of defibrinated blood in vitro.** HENRI FREDERICQ. *Compt. rend. soc. biol.* 88, 625-6(1923). S. MORGULIS

**Researches on the penetration into the interior of the eye of bichloride, cyanide and of salicylarsenate of mercury injected under the conjunctiva.** AUGUSTE VANLINT AND ROBERT WODON. *Compt. rend. soc. biol.* 88, 634-6(1923).—Penetration of the Hg salts into the eye was detd. by a special method for the detection of Hg, which was sensitive to 0.01 mg.  $HgCl_2$  and  $Hg(CN)_2$  were used in concns. of 1:100-1:10000; the Hg salicylarsenate in 0.3-3% solns. The material was injected into the conjunctiva; the aq. humour and the entire eye were examd. for the presence of Hg 1 hr. later. In therapeutic doses Hg did not penetrate at all but with much stronger doses a small amt. of Hg was found in the anterior chamber. S. MORGULIS

**Preliminary study of the effect of magnesium sulfate and of metallic magnesium on metabolism.** RENÉ REDING AND AUGUSTE SLOSSE. *Compt. rend. soc. biol.* 88, 644-6(1923).—Injection of  $MgSO_4$  intramuscularly (70 cc. of a 10% soln.) into a healthy individual causes a diminution in the excretion of total N, uric acid and above all of Cl, while at the same time there is great increase in the Mg excretion. This effect is temporary and a few days later the N and uric acid elimination is again normal; that of Cl, however, remains low. The absorption of metallic Mg has similar effects, as was found in expts. with rabbits with metallic Mg strips placed under the skin. In a patient suffering from cancer of the rectum injections of  $MgSO_4$  brought about a diminution of the excretion of total N, amino acid N and Cl; the uric acid and creatine were increased and a rise in Ca elimination is observed. In general, therefore, Mg causes a lowering of the N and Cl excretion; of uric acid and creatine only in the normal organism; also a considerable increase in the Ca in the urine and feces. S. MORGULIS

**The effect of levorotary and racemic synthetic adrenalines.** L. LAUNOY. *Compt. rend. soc. biol.* 88, 848-52(1923).—The hypertensive action of the levorotary adrenaline is at least twice as great as that of the racemic. S. MORGULIS

**Mechanism of the hypertensive action of nigrosine.** J. GAUTRELET. *Compt. rend. soc. biol.* 88, 859-63(1923).—Nigrosine produces a slight hyperexcitability of the vasoconstrictor mechanism as is evinced by the constriction of the kidney, but it also acts as a parasympathetic excitant. S. MORGULIS

**Effect of geneserine on salivary and pancreatic secretion.** M. POLONOVSKI AND P. COMBEMALE. *Compt. rend. soc. biol.* 88, 881-3(1923).—The alkaloid geneserine has an excito-secretory action on the salivary and pancreatic glands. S. MORGULIS

**An interference phenomenon in the actions of chemotherapeutic substances in experimental trypanosome infections.** C. H. BROWNING AND R. GULBRANSON. *J. Path. Bact.* 25, 395-7(1922).—When parafuchsin is present in the tissues it interferes with therapeutic action of aminoacridine. This was demonstrated in mice infected with a strain of nagana trypanosomes. JOHN T. MYERS

**Fatal poisoning by sodium fluosilicate.** M. SOMMELET. *Bull. sci. pharmacol.* 30, 211-6(1923).— $Na_2SiF_6$  used as an insecticide was accidentally mixed with flour and

the food made therefrom gave rise to 2 cases of poisoning (one fatal). The toxicological study is reported in detail.

L. W. RIGGS

**Use of the carbon arc light in the prevention of rickets.** A. F. HESS AND L. J. UNGER. *J. Am. Med. Assoc.* 78, 1596-8(1922).—The treatment (described in detail) resulted in a rapid subsidence of the signs of rickets accompanied by a const. increase in the inorg. phosphates of the blood. Attempts to cure rickets by adding  $K_2HPO_4$  to ordinary diet were unsuccessful, but it is thought that previous administration of phosphate hastened the cure by C light.

L. W. RIGGS

**Therapeutic use and toxicity of picric acid with a report of two toxic cases.** G. T. PACK. *J. Ind. Hyg.* 4, 501-6(1923).—A review of the use of picric acid as a remedy for burns is given, its action as an antiseptic being rational. The physiol. dose is 0.033 g. Doses of 1 to 2 g. are decidedly toxic with symptoms referred to gastro-intestinal, nervous, circulatory or urinary systems. In industries using or making picric acid the latter is classed as an industrial poison since inhalation of its dust irritates the respiratory and buccal membranes. It may be the etiological factor in many occupational dermatoses. Two cases are reported in which poisoning followed the treatment of burns with picric acid.

L. W. RIGGS

**Arsenobenzene treatment of syphilis.** L. W. HARRISON. *J. State Med.* 31, 177-82(1923).—This subject is discussed from 4 aspects of the arseno-benzene treatment, viz., (1) the efficiency of the preps. most commonly used in the out-patient department and the consulting room, (2) avoidance of toxic effects, (3) adjuvant treatment, (4) extent to which arsenobenzene should be used in the treatment of syphilis in its various stages.

L. W. RIGGS

**Asphyctic hyperchloremia.** KUMAO YAMAKAMI. *Tohoku J. Exptl. Med.* 3, 352-61(1922).—Expts. with 33 dogs under varying conditions showed without exception that the Cl content of the blood was increased and that of the tissues decreased during suffocation.

L. W. RIGGS

**Hyperglucemia and glucosuria caused by ammonium chloride and by magnesium sulfate in cats.** SACHIKADO MORITA. *Tohoku J. Exptl. Med.* 3, 363-413(1922).—Subcutaneous administration of  $NH_4Cl$  or  $MgSO_4$  causes hyperglucemia and glucosuria in normal cats lasting several hrs., but not detectable on the next day. The accompanying reactions were paradoxical dilatation of pupils, lowering of the body temp., and generally an accelerated respiration which continued for a much shorter time than the hyperglucemia or pupil dilatation. Tests with cats in which the salt soln. was injected into a deafferent hind foot gave the same results. With bilateral splanchnectomy,  $NH_4Cl$  fails to cause the above-mentioned reactions, while  $MgSO_4$  causes a reduced hyperglucosuria and respiratory acceleration but the pupil dilatation is not lessened and the lowering of the body temp. is unaffected. The respiratory acceleration stands in no causal relation to the hyperglucemia but each may have its origin in the respiratory center of the sugar-forming organ or organs.

L. W. RIGGS

**Fate of arsenic after intravenous and intrathecal injection.** R. D. RUDOLF AND F. M. R. BULMER. *Am. J. Med. Sci.* 165, 47-53(1923).—By application of the Gutzzeit test to the tissues of rabbits after the injection of phenarsenamine (arsphenamine) it was shown that after intravenous injection little, if any, As reaches the central nervous tissue, and after intrathecal injection, in therapeutic doses, none can be detected in the spinal cord.

G. H. SMITH

**Tolysin in acute rheumatic fever and other conditions.** H. G. BARBOUR, E. LOZINSKY AND C. CLEMENTS. *Am. J. Med. Sci.* 165, 708-18(1923).—Tolysin (ßt p-tolylcinchoninate) is efficient in the therapy of acute rheumatic fever and is of some benefit in other forms of arthritis. The drug has an antipyretic action, and is absorbed by the body in amts. but slightly above the therapeutic dose.

G. H. S.

**"Tonic" contraction of striated mammalian muscle after exclusion of the motor nerves.** II. **Muscles of the extremities.** E. FRANK, M. NOTHMANN AND H. HIRSCH-KAUFFMANN. *Arch. ges. Physiol. (Pflüger's)* 198, 391-400(1923); cf. C. A. 17, 2010.—The normal cat or dog manifests no motor reactions when injected with 2 mg. of acetylcholine or nicotine. If the same amt. of these substances is injected, either intravenously or intra-arterially, into these animals after section of the lumbar or sacral roots a "tonic" contraction of the lower extremities takes place with a hardening of the entire area. The rigidity persists for 30 sec. and then disappears slowly, but completely. The phenomenon is not induced if there has been a preliminary treatment with scopolamine or novocaine. Acetylcholine or nicotine injected into either vein or artery 4 to 6 days after section of the peripheral nerves produces a slow motion and contraction of the muscles supplied by these nerves. This reaction persists for about 5 min. Scopolamine, novocaine, or adrenaline suppresses this reaction also. The reactions induced in the



extremities after exclusion of the motor nerves correspond to those previously observed in the tongue.

**Intravenous narcosis in 850 cases.** A. LEHRNBECHER. *Arch. Min. Chir.* 123, 317-29(1923).—A discussion of the results secured in 850 cases with narcosis induced by intravenous isopropyl-ether administration.

**Carbon monoxide intoxication.** R. JAKSCH-WARTENHORST. *Med. Klin.* 19, 11-4(1923).—Intoxication with CO causes an increased temp. even though pulmonary complications, such as pneumonia, do not develop. The blood pressure falls, the red and white cells increase in number, carbohydrate metabolism is disturbed, and in all cases observed clinically there is involvement of the nervous mechanism.

**Constancy of blood groups in man: effect of therapeutic agents on blood groups.** KURT MEYER AND HEDWIG ZISKOVEN. *Med. Klin.* 19, 87-9(1923).—Narcosis, treatment with Ra or with Röntgen rays, or the administration of such substances as caffeine, digitalis, As, quinine, and salicylates does not modify the blood group as has been reported by Edens. The changes observed by this author were not agglutinative changes but were rather alterations in sedimentation rates and an increased tendency to rouleaux formation.

**Experimental pharmacology of the male genital tract. VII. Oleum santali.** ALFRED PERUTZ. *Med. Klin.* 19, 348-50(1923).—The ethereal oils, particularly oleum santali, do not exert a definite bactericidal effect upon gonococci in the urogenital tract.

**Direct retention of inorganic iron in perfusion of the surviving liver.** MATSUOKA. *Med. Kim.* 19, 351-2(1923).—The surviving liver of rabbits was perfused with Fe-contg. mineral water. The total Fe content of the perfusion fluid was reduced from 2.07 to 1.21 mg. (av.).

**The excretion of ethereal sulfates by rabbits after feeding phenol, bromophenol and bromobenzene.** H. RHODE. *Z. physiol. Chem.* 124, 15-36(1922).—Where phenol (0.2 g. per kg.) was administered simultaneously with cystine, taurine and  $\text{Na}_2\text{SO}_3$  the percentages excreted as ethereal sulfate were 33%, 17% and 27%, resp. The 3 compds. were given in such amts. as to provide 3 S atoms for each PhOH mol. except in the last case, when 2 S atoms were furnished. Inorg. sulfates and thiosulfate were without influence. The 2 Br compds. appear partly as ethereal sulfates, but when cystine is given simultaneously they appear as mercapturic acid.

**Nascency as an intensifying force in therapeutics. II.** G. LUNAN. *Pharm. J.* 110, 384-5(1923); cf. *C. A.* 14, 2969.—Very good therapeutic effects are obtained when the remedy, e. g.  $\text{HClO}$ ,  $\text{CO}_2$ , S, I,  $\text{BiO}$  salt, is made to act in the nascent state. The components of the reaction, e. g.,  $\text{NaClO}$  and  $\text{H}_3\text{BO}_3$ ,  $\text{NaHCO}_3$  and  $\text{HCl}$ , KI and  $\text{Cl-H}_2\text{O}$ , each in suitable pharmaceutical combination, are applied or ingested consecutively; nascent S in ointments may be formed by the slow interaction of  $\text{Na}_2\text{S}_2\text{O}_3$  with boric and salicylic acids. The KI-Cl method is preferable to the use of tincture of I.

**Rhododendron poisoning.** S. W. HARDIKAR. *J. Pharmacol.* 20, 17-44(1922).—Andromedotoxin, the active principle of the rhododendron, acts upon the terminations of the vagus which it 1st stimulates and then paralyzes; this explains some of its most prominent effects. It paralyzes the motor nerve ends in striped muscle, has a narcotic effect upon the higher centers in the brain but does not affect the spinal cord. In very large doses death is due to a direct action upon the heart while with smaller doses it is due to failure of the respiration. The poison has a slight vaso-constrictor effect of peripheral origin upon the blood vessels. Involuntary muscle which is not supplied by the vagus is not affected. The seat of the emetic action of the poison has not been determined. The increased secretion of saliva is probably only the 1st stage of the emetic action and is not due to a specific effect upon the salivary glands or their secretory nerves. At least  $\frac{1}{2}$  of the poison injected hypodermically leaves the body unchanged in the urine.

**Pharmacology of sodium citrate. I. The influence of sodium citrate on respiration and circulation.** WM. SALANT AND NATHANIEL KLEITMAN. *J. Pharmacol.* 20, 481-97(1923).—Small and medium doses of Na citrate injected intravenously usually stimulate respiration in all animals. Only a slight fall of blood pressure was observed in dogs under anesthesia, but in cats a fall of 30 to 60% may occur. After intramuscular injections of large doses of citrate the fall of blood pressure was gradual.

**Action of camphor, menthol and thymol on the circulation.** R. ST. A. HEATHCOTE. *J. Pharmacol.* 21, 177-90(1923).—Camphor, thymol and menthol depress the isolated heart of both the frog and the rabbit directly, acting on the cardiac muscle. All 3

dilate the coronary vessels. In anesthetized animals, camphor, however given, does not cause a rise of blood pressure, if the dose is not sufficient to cause convulsions. Similarly, after the cerebral hemispheres are removed, no rise in blood pressure occurs even with doses up to 1 g. per kg. There is no convincing pharmacol. evidence that camphor possesses any value whatever as a cardiac or circulatory stimulant. Its value, if any, for this purpose in man should be established or disproved by more exact clinical observations. Thymol, of intermediate soly., is the most toxic and has the greatest effect on the blood pressure.

C. J. WEST

## I—ZOOLOGY

R. A. GORTNER

Cell metabolism in the insect fat-body. I. Cytological changes accompanying growth and histolysis of the fat-body of *Apis mellifica*. G. H. BISHOP. *J. Morphology* 36, 567-601 (1922).—Histological study indicates that the partially digested food of the early larva, the "royal jelly" elaborated by the worker bees, contg. carbohydrate, fat, and protein, is fed the queen larva throughout larval growth, while after the 3rd day the worker is fed considerable amts. of honey and undigested pollen, and the male still more pollen. The fat and practically all the carbohydrate taken up by the fat-body are stored as fat-droplets until, at the beginning of metamorphosis, these droplets are worked over into the "albuminoid globules" developed from granules from the nucleus. These globules represent the cell element in which the chem. transformations of the cell constituents take place in prepn. for tissue use.

A. T. CAMERON

Temporary concentration of sea salts about *Arbacia* eggs. OTTO GLASER. *Biol. Bull. Marine Biol. Lab.* 43, 175-83 (1922).—*Arbacia* egg-secretion temporarily lowers the sp. gr. of sea water and prevents standardizing the egg secretion by methods depending on surface tension, viscosity or sp. gr. The mechanism by which these deficiencies are brought about is the chorion, since eggs deprived of their jelly by shaking do not cause a salt deficit. Localization by means of 0.1 N  $\text{AgNO}_3$  in the presence of  $\text{HNO}_3$  shows a concn. of Cl about the eggs. This is temporary, since the chorion within a few hrs. undergoes disintegration in sea water. As a result of this the salts are dispersed and the sp. gr. of the sea water may return to normal. A rise above normal may be attributed to the presence of exudate in soln.

L. W. RIGGS

Acceleration of the rate of cell division. A. RICHARDS. *Biol. Bull. Marine Biol. Lab.* 43, 348-66 (1922).—Expts. on the eggs of *Haminea virescens* show that the eggs may be induced to undergo cleavage at an accelerated rate by the following reagents: 0.004 to 0.009% NaOH, 0.006 to 0.009%  $\text{NH}_4\text{OH}$ , 0.006 to 0.017% KOH, thyroid ext. and pilocarpine-HCl in weak concns.  $\text{Ba}(\text{OH})_2$ ,  $\text{Cr}(\text{OH})_3$ , and pilocarpine nitrate cause no acceleration. The acceleration of cleavage is not always followed by continuously quickened development, for in some cases the exptl. eggs do not hatch ahead of the control. It is suggested that the agencies which are capable of accelerating division bring about this result through their property of influencing the enzymes of the cells, the setting free and activation of which are correlated with the mitotic processes.

L. W. RIGGS

Copper, enzymes and fertilization. OTTO GLASER. *Biol. Bull. Marine Biol. Lab.* 44, 79-103 (1923).—If a soln. contg. 1 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per l. is added to sea water about 37% of the Cu is pptd., probably as insol. basic carbonates. The sea water retains about 0.174 mg. of Cu per cc., the equiv. of  $M/365$  or  $N/730$ . Two-tenths cc. of normal *Arbacia* eggs in 75 min. reduces the concn. of 14.8 cc. of a Cu soln. from  $N/1460$  to  $N/1790.9$ . In this reduction the egg jelly or chorion is heavily involved. It is impossible to det. the amts. of Cu absorbed by normal eggs and eggs without jelly because of an apparent secretion of Cu by the eggs themselves. Cu was localized in the egg directly by means of hematoxylin and by the triple-nitrite of K, Cu and Pb. Indirectly it was localized by the analysis of the egg secretions. Cu occurs chiefly in the egg pigment. The vitelline membrane and the chorion also contain Cu. It is not a regular constituent of agglutinin ppts., but was found constantly in ppts. of lipolysis, showing that both Cu and the enzyme are located in the cortex of the egg. The association of Cu with lipolysis is not an isolated case, it was also found in preps. of pancreatic enzymes and in pepsin. In eggs exposed to  $N/180$  Cu soln. for 20 min. the Cu is widely diffused through the cytoplasm and concd. in the chorion, the vitelline membrane and the cortex. One cc. of unripe ovarian *Arbacia* eggs normally contains  $17\mu\text{g.}$ , ripe shed eggs  $175\mu\text{g.}$ , and fertilized eggs  $21\mu\text{g.}$  of Cu. An attempt is made to account for the function of Cu in eggs during development, and for the elimination of Cu-bearing pigment during fertilization.

L. W. RIGGS

Reversibility of the phenomena of arrest by lowering of  $p_{\text{H}}$  in the evolution of the

eggs of sea urchin. M. ROSE, J. DRAGOIU AND F. VLĂȘ. *Compt. rend.* 176, 531-4 (1923); cf. C. A. 17, 1674.—Changes in development of the egg for  $p_H$  values ranging from 3 to 8 are described. Four modes of reaction may be distinguished, and by plotting  $p_H$  values against time of sojourn in hrs., zones of total irreversibility with  $p_H$  3 to 5 and of reversibility with  $p_H$  5 to 8 are shown with a narrow zone of cytolytic evolution between them. The test of total irreversibility is furnished by the appearance of the *paquet noir* indicating a pyocyanic state, probably resulting from perturbations of the charges of the chromosomes.

L. W. RIGGS

The ostrich egg-shell—its chemical composition and microstructure. WM. TORRANCE. *J. S. African Chem. Inst.* 6, No. 1, 11-17 (1923).—Analyses of North and South African shells gave practically the same results, as follows:  $SiO_2$  0.06,  $Al_2O_3$  +  $Fe_2O_3$  0.13,  $CaCO_3$  95.74,  $MgCO_3$  2.14,  $Ca_3(PO_4)_2$  0.44, protein 1.10, water 0.34, sum 99.95. No aragonite was present by the  $Co(NO_3)_2$  test. The shell is composed of 2 layers, an inner layer of structureless  $CaCO_3$ , and an external layer of minute calcite prisms with their long axes perpendicular to the bounding surface, in this case the oviduct.

L. W. RIGGS

Animal light. LOESER. *Umschau* 27, 86-8 (1923).—A review of the work of P. Buchner (cf. C. A. 16, 2336), Pierantoni and others.

L. W. RIGGS

Disturbances of inheritance in echinoderm larvae by ammonia. WALTER LANDAUER. *Arch. Entwickl. Organ.* 52, 1-94 (1922).—The bastard larvae from the eggs of *Sphaerechinus granularis* and the sperm of *Strongylocentrotus lividus* follow an atypical development when the eggs are subjected to a sea water contg.  $NH_3$ .

G. H. S.

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The earning power of research. As exemplified in the baking industry. I. K. RUSSELL. *Ind. Eng. Chem.* 15, 645-7 (1923).

E. J. C.

Pectin, jelly-making and sugar. L. H. CHERNOFF. *Am. Food J.* 18, 200-1; *Facts About Sugar* 16, 336 (1923).—A general discussion of pectin and its role in jelly-making with relation to sugar.

H. A. LEPPER

Determination of copper in greened legume preserves. E. JASAUSS. *J. pharm. chim.* 27, 290-8 (1923).—Incinerate, dissolve the Cu, then det. it electrolytically or iodometrically (C. A. 14, 34; 17, 1400). To det. Cu in preserved spinach, incinerate after previous treatment with a soln. of  $Mg(NO_3)_2$  and  $HNO_3$ , dissolve the Cu in 33%  $H_2SO_4$ , remove excess by evapn., dissolve in 5%  $H_2SO_4$ , ppt. the Cu with Al foil and continue as in the usual iodometric method. To detect traces of Cu in the insol. ash, fuse with  $NaHSO_4$  and det. the Cu colorimetrically.

S. WALDBOTT

Copper sulfate in tinned peas. P. A. PANTON. *Pharm. J.* 110, 393-4 (1923).—Prolonged digestion *in vitro*, first with strong gastric juice, then with trypsin, of peas contg. somewhat less than 2 grains of Cu to the lb., failed to bring more than traces of Cu into soln. by means of gastric juice, none with trypsin. In both cases, the bulk of Cu remained insol. and undigested. The results were used as medical evidence.

S. WALDBOTT

Dried bananas. C. H. WRIGHT. *Tropical Agriculturist* 60, 53-6 (1923).—The analysis of a green banana pulp showed  $H_2O$  68.8, protein 0.0, oil 1.1, carbohydrate 28.7, fiber 0.3, ash 1.1%. Flour prepd. by grinding dried banana chips showed the following compn.:  $H_2O$  11.10-14.21, protein 2.69-4.0, fat 0.22-0.83, carbohydrate 79.04-84.83, fiber 0.72-1.50, ash 2.23-2.92, N 0.11-0.43%.

M. S. ANDERSON

Chemical changes during the process of the ripening of the mango fruit. V. G. PATWARDHAN. *J. Proc. Asiatic Soc. Bengal, Proc. 8th Indian Sci. Cong.* 17, 88-9 (1922).—During the ripening of mangoes in the dark, their temp. increases approx. 8°, the acidity is reduced to approx. 25% of the original, the reducing sugars remain 1-5% and the non-reducing sugars increase from a low % to 55-65% of the dried juice.

C. C. DAVIS

Experiments with *Bacillus (Clostridium) botulinus* under household conditions. RUTH B. EDMONDSON, CHARLES THOM AND L. T. GLTNER. *Am. Food J.* 18, 143-6 (1923).—Studies were made with *B. botulinus* on various foods including milk, meat and bread to det. the effect of household storage conditions on the development of the toxin in such foods. In general the expts. indicate that food held in a reasonably efficient ice box from 1 to 2 days is practically free from development of *B. botulinus* even if present and is entirely safe for ordinary recocking. Food held 3-4 days if show-

ing no phys. signs of spoilage such as mold, scum, souring or odor involves little actual danger, but in every case calls for thorough recocking. The need of some type of effective refrigerator or cooling device in all households is clearly shown.

H. A. LEPPER  
**Aropy milk organism isolated from the Finnish "Piima" or "Fili."** HAROLD MACY. *J. Dairy Sci.* 6, 127-30 (1923).—Results are given of a detailed study of an organism isolated from this beverage. Characteristic of the organism is its failure to grow well on ordinary routine media, its ability to produce marked, persistent ropiness in milk and its resistance to desiccation and heat. It is suggested that it be given as a new species, *Streptococcus piima*. O. L. EVENSON

**Pasteurized vs. clean milk.** C. W. HUNT. *J. Roy. San. Inst.* 42, 52-8 (1921); *Abstracts Bact.* 6, 231.—A consideration of the pasteurizing process covering in a general way the attendant bacterial reduction and the probable effect on vitamins, and calling attention to irregularities of pasteurization where carelessly or insufficiently conducted. H. G.

**Coagulation of milk by acid.** LEONARD ANDERSON. *Trans. Faraday Soc.* (advance proof) 1923.—A study of the effect of acid and alkali on the pptn. of casein with the object of obtaining information as to its behavior and protective action towards the fat globules. On addition of HCl to milk of various dilns. the pptn. increases with increasing amts. of acid until a max. rate of settling occurs, the amt. of acid required being inversely proportional to the diln. of the milk. The fat globules are carried down with the curd. If sufficient acid is added the casein goes into soln. and the globules rise to the surface but remain uncoalesced. If more acid is added the casein is again pptd. This is considered a salting out of casein chloride by HCl. 0.1 N NaOH does not bring about coalescence of the globules. Emulsions of benzene and olive oil in casein soln. behave like milk in respect to acid and alkali. It is concluded that casein is a protective agent for the particles of fat in milk, the globules being able to coalesce only when the excess protein surrounding them has been removed. The microscope was used in observing the globules. Three tables are given. O. L. EVENSON

**Sterol content of cow milk.** F. W. FOX AND J. A. GARDNER. *Biochem. J.* 17, 94-102 (1923).—The sterol in milk which can be pptd. by digitonin forms only about  $\frac{1}{3}$  to  $\frac{1}{2}$  of the total unsaponifiable matter of the fat. B. HARROW

**Sodium hypochlorite.** Some studies on the bactericidal action of sodium hypochlorite in cow milk. H. F. ZOLLER AND SYLVIA M. EATON. *J. Dairy Sci.* 6, 131-6 (1923).—A table is given showing the effect on bacterial flora of adding NaOCl corresponding to an available Cl content of 0.00001 to 0.1% in the milk for different periods of contact. It is concluded that NaOCl has a relatively low bactericidal effect on milk. Only when an excess of NaOCl was present was more than 50% reduction in plate count obtained. The presence of the org. matter in the milk seemed to protect the vitality of the organisms as regards their power to reproduce on a milk agar plate even after exposure to an excess of NaOCl. O. L. EVENSON

**The alcohol test as a means of detecting abnormal milk.** A. C. WEIMAR. *J. Dairy Sci.* 6, 95-101 (1923).—Three tables are given showing results of exptl. tests on individual cows from 3 different herds whose milk reacted positively to the alc. test. The fermentation test, alc. test, bacterial count, acid test and flavor and odor are given. These exptl. tests gave no clue as to the cause of variation in positive or negative results. Visits to the farms, however, showed that the positive reactors were fed moldy silage. Cows refusing silage reacted negatively. The relation of the alc. test to the coagulating point of evapd. milk was also shown by running the milk from 3 of the cows used in the feeding test, through a lab. condenser. It was shown that the positively reacting milk had a lower coagulating point than milk reacting negatively to the alc. test. It is concluded that the alc. test is of value in detecting some cases of abnormal milk which could not be detected by chem. analysis. O. L. EVENSON

**Determination of the total protein content of milk in the Dutch East Indies by means of the formaldehyde number.** J. F. A. POOL. *Pharm. Weekblad* 60, 419-28 (1923).—The  $\text{CH}_2\text{O}$  no. is the no. of cc. of 0.25 N alkali required to neutralize 100 cc. of milk previously neutralized to phenolphthalein and treated with 20 cc. of neutral formalin. This no.  $\times$  the factor 0.495 = protein. The detn. agrees within 0.2% with the Kjeldahl detn. For practical purposes the factor may be considered 0.5. The method is used mainly by the military pharmacists. A. W. DOX

**Determining solids-not-fat in cow milk.** BENJAMIN MASUROVSKY. *J. Dairy Sci.* 6, 145-9 (1923).—From data compiled by Shaw and Eckles (*C. A.* 5, 3597) M. computes the coeffs. of variability in detg. the solids not fat in normal cow milk by the

Babcock formula to be as follows: Jersey milk 0.9925; Holstein 0.9917; Ayrshire 0.9955; Shorthorn 0.9890; mixed breeds 0.9922. The mean deviation, derived from a comparison of the results obtained by the use of the Babcock formula and by gravimetric means, was found to be  $+0.0604$ . To come within very close approximations to the chemically detd. values for solids-not-fat in normal cow milk, the following formulas should be used: (a) s. n. f. =  $[(L/4) + 0.2 f] \times 0.9922$  or (b), s. n. f. =  $[(L/4) + 0.2 f] - 0.0604$ , where  $L$  = lactometer reading in Quevenne degrees, and  $f$  = % of butterfat. A frequency curve is given, plotted from the number and size of deviations.

O. L. EVENSON

**The Hoyberg process for the determination of fat in milk and cream.** ORLA-JENSEN. *Løst* 3, 177-87(1923).—The Hoyberg method (*C. A.* 15, 279) is compared with the Roesse-Gottlieb and Gerber methods on the same samples of milk and cream. Cow milk taken during the early period of lactation, and also cow milk taken during the later period of lactation, are compared. The Hoyberg method agrees very well with the Roesse-Gottlieb method on all samples of milk examd. The Gerber method gave uniformly higher results than the Roesse-Gottlieb. In cream the Hoyberg method is greatly superior to that of Gerber's. Importance is attached to the fact that the Hoyberg method does away with the employment of the expensive centrifugal machine necessary in the operation of the Gerber method.

H. F. ZOLLER

**The influence of the physical state of the fat upon the process of butter formation.** W. VAN DAM. *Offic. Org. Algem. Nederl. Zuivelbld.* No. 855, 1856, 1857(1922); *Milchw. Zentr.* 52, 1-4(1923).—Expts. to show the effect of temp. on the process of butter formation show that this effect changes according as the cream is cooled to a greater or less degree. The % fat in the buttermilk is lowest if the cream has been cooled so that the fat has reached a state of equil. The acidity of the cream has little effect.

O. L. EVENSON

**Acidity of butter and its by-products.** F. W. BOUSKA. *J. Dairy Sci.* 6, 122-6(1923).—A discussion of the acidity of cream, butter and buttermilk and method of churning.

O. L. EVENSON

**The microbial content of butter.** G. DALLA TORRE. *Ann. Ist. Sper. Caseifici, Lodi* 1, 155-70(1922); *Abstracts Bact.* 6, 450.—T. calls attention to the very diverse figures which appear in the literature as to the no. of bacteria in butter. The no. of germs contained in a g. of butter vary from a min. of 36,000 to a max. of 7,000,000. This great variation in the microbial content is due partly to the influence of different temps., and different periods of churning and partly to varying temps., at which the milk is kept, and also more or less to prolonged holding of the milk before sepg. Of the various bacteria found in the analysis the lactic acid organisms were always found in the greatest numbers varying from 29,000 to 7,000,000. Organisms of the coliaerogenes type were found very frequently but not in large numbers. Gelatin liquefiers and yeasts were also found in considerable numbers as well as *Oidium lactis*. Anaerobic bacteria were found in several samples of butter, generally present in quite small numbers. In order to determine them it was necessary to pasteurize the butter for analysis.

H. G.

**The water content of margarine.** KURT BRAUER. *Chem.-Ztg.* 47, 113-5(1923).—A study of the  $H_2O$  content of margarine and the effect of compn., process of manuf. and sampling thereon. The requirement of 16%  $H_2O$  as a max. in salted margarine can be met. Interpretation must be made on an av. sample. (Cf. *C. A.* 17, 157.)

H. A. LEPPER

**Dried yeast, fish meal, and alkaloid-free lupines.** GERLACH. *Mitt. deut. Landw.-ges.* 38, 99-100(1923).—The compn. of these materials is given and their relative values as animal feeds are discussed.

K. D. JACOB

**The conservation of protein in the removal of the bitter principle of lupines.** GOY. *Mitt. deut. Landw.-ges.* 38, 108-9(1923).—In prep. lupines as food for stock the usual practice is to remove the bitter alkaloids by washing first with cold and finally with hot  $H_2O$ . During this process a loss of about 14% of the total protein occurs owing to the soly. of these compds. in cold  $H_2O$ . By treating the lupines with boiling  $H_2O$  and steam the protein compds. are coagulated and the loss is reduced to about 6% of the total protein. The amt. of alkaloid removed is about the same with both processes. Lupines treated only with steam at 1.5 atm. pressure remain hard and shriveled, and the alkaloid content is not sufficiently reduced to prevent injury when fed to stock.

K. D. JACOB

Biological action of nital and its significance for the hygiene of food (BART) 11C.

Adaptation of the iodometric aldose determination to the analysis of mixtures containing carbohydrate (KOLTHOFF) 7.

KLING, A.: Méthodes actuelles d'expertises employées au Laboratoire Municipal de Paris et documents sur les matières relatives à l'alimentation. II. Matières grasses, beurre, cires et paraffine, essence de térébenthine, huiles minérales. Paris: Dunod. Reviewed in *Ann. fals.* 16, 113(1923); *Mat. grasses* 14, 6327-8(1922).

Powdered milk. C. S. STEVENS. U. S. 1,453,859, May 1. Milk to be desiccated is homogenized and then immediately subjected to the action of steam at atm. pressure to evap. moisture and coagulate albumin of the milk in the form of a dry sheath surrounding the fat globules of the milk.

"Greaseproofing" fibrous receptacles for foods. W. L. WRIGHT. U. S. 1,454,421, May 8. Coconut oil emulsified with gelatin and H<sub>2</sub>O is used for greaseproofing fibrous receptacles.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Chemistry-commerce course at the University of Wisconsin. J. H. MATHEWS. *Science* 57, 549-50(1923). E. J. C.

The new chemical engineering laboratory at the University of Michigan. A. H. WHITE. *Ind. Eng. Chem.* 15, 843-4(1923); illus. E. J. C.

Dermatosis following the use of cutting oils and lubricating compounds. Wm. J. MCCONNELL. *U. S. Pub. Health Repts.* 37, 1773-94(1922); *Abstracts Bact.* 6, 454. H. G.

Dangers of and treatment for carbon monoxide poisoning. R. R. SAYERS AND W. P. YANT. U. S. Bur. of Mines, *Repts. of Investigations* No. 2476, 11 pp.(1923); cf. *C. A.* 16, 1276, 2918. E. J. C.

Gas masks in chemical plants. I. V. KEPNER. *Natl. Safety News* 7, 31(1923).—The various types of app. in use prior to and since the World War are discussed. E. J. C.

Chemistry in future warfare. J. H. HILDEBRAND. *Calif. Eng. Mar.* 1923; *Chem. Warfare* 9, No. 3, 2-3(1923). E. J. C.

The value of cost accounting in analytical and consulting laboratories. F. W. FEUERBACHER. *Science* 56, 537-8(1923); cf. *C. A.* 17, 443. E. J. C.

The X-ray examination of materials. A. G. WARREN. *Electrician* 90, 421(1923).—A review. C. G. F.

Methods of air drying. E. C. HOLDEN. *Chem. Met. Eng.* 28, 801-4(1923).—The 4 types of methods for drying air on an industrial scale are (1) by reagents, (2) by compression, (3) by refrigeration, (4) by adsorption. H. discusses each of these types, illustrating in greater detail type (1) by H<sub>2</sub>SO<sub>4</sub>, and type (4) by silica gel. Several charts and also a diagrammatic lay-out of a continuous three-stage counter-current gel adsorption plant are given. E. G. R. ARDAGH

The viscosity of lubricating oils at low temperatures. MASATOSHI OKOCHI AND MASAICHI MATJIMA. *Rikugaku Kenkyujo Ihô* 2, 23-37(1923).—A glass capillary tube (10 cm. long) is fused to a small glass ball and then connected to a large bottle (B) and a Hg manometer (C). The capillary and the ball (A) are immersed in the lubricating oils to be examd., the latter being cooled by a suitable freezing mixt. After evacuating B, A is connected to B, and the time it takes to fill the ball with oils through the capillary is measured. When the viscosity of the oil became large, the oil is previously filled into A, and then the content is drawn away by the compressed air in B. From these data, the viscosity was calcd. by the formula,  $\eta = (\pi R^4/8VT)(P_e - P_i)$ , where R = radius of the capillary, V = vol. of oil flowed through the capillary, l = length of the capillary, and P<sub>e</sub> and P<sub>i</sub> = pressures of the oil at the exit and entrance, resp., of the capillary. The results are given in tables and diagrams, temp. being from 27° to -18°. The oils used for the investigation were as follows: (1) rape seed, (2) gingell, (3) refined rape seed, (4) camelli, (5) mobile, (7) spindle, (8) whale, (9) olive, and (10) machine-oils, (11) petroleum, (12) liquid paraffin, (13) 90% whale oil + 10% petroleum, (14) 80% whale oil + 20% petroleum, (15) 90% machine oil + 10% petroleum, and (16) 50% liquid paraffin + 50% petroleum. The chem. properties of the oils are not given. The increase of viscosity according to

lowering of temp. is almost expressed by a hyperbola. So the consts. ( $\alpha$ ,  $a$ , and  $b$ ) for the oils were calcd. from the formula:  $\eta = [a/(T-b)]^1/\alpha$ ,

	$\alpha$ .	$a$ .	$b$ .
(1)	0.1	200.7	85.0
(2)	0.1	204.4	69.6
(3)	0.3	105.1	180.4
(4)	0.09	216.3	66.2
(5)	0.09	122.8	174.7
(7)	0.50	21.56	235.8
(8)	1.10	7.8	260.3
(9)	0.2	98.5	181.8
(10)	0.4	53.4	253.9
(11)	0.8	4.18	241.5
(12)	0.5	39.4	241.6
(13)	2.0	1.5	263.1
(15)	0.5	35.2	249.7
(16)	0.6	206.8	157.6

The calcd. results from the formula almost coincide with exptl. results; but in whale, gingell, and soy-bean oils, it is not coincidental at low temp.; some critical temp. is observed, which is due to the formation of solid particles. Petroleum has no great effect on the viscosity by the decrease of temp. The viscosity of (14) at  $-3^\circ$  is equal to that of (13) at  $6^\circ$  and (16) is a liquid at even  $-60^\circ$ . K. KASHIMA

**Evaporation by compression.** W. GENSECKE. *Chem. Met. Eng.* 28, 448-56 (1923); *Z. Ver. deut. Ing.* 67, 249-55.—The function of the compressor is not to generate the heat required for evapn. but to raise the temp. of heat already available so that the necessary thermal head is obtained. By ignoring heat losses multiple effect and compression evapn. are compared theoretically; the latter is less efficient by the product of the efficiencies of the compressor and its driving machine. Such a comparison may involve an impossible no. of effects depending on the thermal head required for evapn. A chart presents this comparison, steam consumption per unit evapn. vs. thermal head required. Compression evapn. becomes economical as thermal head required decreases. The above is modified in practice by coupling thermal processes, examples of which are given, the above chart being repeated for the case of engine exhaust furnishing the steam for evapn. Compression evapn. becomes less favorable under these conditions. If in addition all the exhaust steam from the evaporator is used for general heating purposes, optimum economy is obtained, and no gain can be made by compression evapn. As a practical example of this coupling of thermal processes, the *manuf. of raw beet sugar* is discussed. The steam consumption for an Austrian factory working 1,500,000 kg. beets per day is, per 100 kg. beets worked: 2.7 kg. for generation of energy, 5.2 kg. for primary evaporator, 13 kg. for secondary evaporator, 28 kg. for diffusion and heating purposes, and 8 kg. for radiation, total 56.9 kg. Various means of reducing the overall steam consumption are available particularly by compression applied to the vapors available from the *beet shavings dryer* in which 6 kg. coal is consumed per kg. dried shavings. The reduction is, however, small, about 4 kg. per 100 kg. beets. The field of compression evapn. is limited. It possesses advantages when (1) objectionably high pressures would be required in the first stages of multiple effects; (2) low and constant temps. are required by the nature of the solns. being handled; (3) the b. p. rise with concn. is small; (4) a use for exhaust steam exists whose temp. can be made independent of evapn. temp. Examples of *milk* and *fruit juice* evapn. plant are given to illustrate these conditions. In the *former*, electrically operated, 53.5 kg.  $H_2O$  are evapd. per kw. hr. Either piston, turbo or injector compressors may be used, piston being of low efficiency and small capacity, turbo and injector being of good efficiency and large capacity. Characteristics of the three types are given. C. C. HERITAGE

**Laws of crushing.** J. HERMAN. *Eng. Mining J. Press* 115, 498-9 (1923).—Tests on a wide variety of materials, with a screen discharge ball mill, are presented as curves; energy input vs. mesh of product with *Kick's* and *Rittinger's* laws are also shown graphically for comparison. The results are more in accord with Rittinger's law, particularly when the grinding is efficiently done. This law represents the min. power required, Kick's the max. Results on tough materials approach the latter law especially when the reduction ratio is small. The error in applying Kick's law to crushing lies in assuming immediate release of pressure after initial fracture and in failing to consider the energy remaining after this initial fracture which does further crushing

work. Rittinger's law also applies to sawing, planing, filing, boring, chiseling, scouring, peeling and gouging. C. C. HERITAGE

The commercial applications of catalysis in organic chemistry. A. MAILHE. *Technique moderne* 15, 257-64(1923).—A review with bibliography covering catalysis by metals, metallic oxides, metallic salts and acids. A. PAPINEAU-COUTURE

Canada's chemical trade. S. J. COOK. *Can. Chem. Met.* 7, 135-9(1923); cf. C. A. 16, 449. E. J. C.

Review of our (Canadian) chemical and allied industries. The general chemical situation. V. G. BARTRAM. The alkali industry. G. M. DUCK. Cobalt, silver and arsenic. F. A. BAPT. *Can. Chem. Met.* 7, 132(1923). The pulp and paper industry. J. N. STEPHENSON. The chemical distributors' outlook. T. E. O'REILLY. *Ibid* 133. The oil industry in Canada. S. R. PARSONS. *Ibid* 134. E. J. C.

The chemico-physical foundation of evaporation and of the solution of mother liquors (KRULL) 2.

FRANCHE, G.: Les huiles en mécanique. Paris: Desforges. 376 pp. Fr. 16.50. Reviewed in *Recherches et inventions* 4, 344(1923).

HOPE, E. W., et al.: Industrial Hygiene and Medicine. London: Bailliere. 778 pp. LARSON, ALF.: Den svenska kemiska industrien. Stockholm: Tullberg's förlag. 316 pp. 48 kr. Reviewed in *Stensk Kem. Tids.* 35, 115-6(1923).

SESTINI, ANTRINO: Corso di chimica industriale. Parte prima (Generalità e metallurgia). Brescia: Giulio Vannini. 509 pp. Reviewed in *Chimie et industrie* 9, 642 (1923).

WALKER, WM. H., LEWIS, WARREN K., and McADAMS, WM. H.: Principles of Chemical Engineering. New York: McGraw-Hill Book Co. 637 pp. \$5. For a symposium review see *Chem. Met. Eng.* 28, 946-50(1923).

Yearbook of the American Engineering Standards Committee, 1923. New York: American Engineering Standards Committee, 29 West 39th St. 48 pp. Reviewed in *Ind. Eng. Chem.* 15, 653(1923).

Removing water from colloidal substances. H. HORST. U. S. 1,455,728, May 15. Colloidal substances such as those of *peat or coal sludge* are freed from water by admixture of adsorbing substances the minimum fineness of which is 0.1 mm. or larger.

Recovery of ether from gases. J. H. BRIGGAT. U. S. 1,455,707, May 15. Ether mixed with alc. vapor and gases such as are evolved in drying *explosives* is recovered by absorption in benzenesulfonic acid or a similar sulfonic acid liquid and sepd. from the absorption liquid by redistn.

Refrigerant. F. W. ANDREWS. Can. 230,306, Apr. 10, 1923. A refrigerant contains SO<sub>2</sub> mixed with about 0.5% CO<sub>2</sub> to increase the latent heat of evapn. without material increase of pressure and 2.5% of CCl<sub>4</sub> to keep the SO<sub>2</sub> and CO<sub>2</sub> in combination and afford lubrication.

Lubricating mixture. C. VERNIAUD. U. S. 1,454,002, May 1. A lubricant adapted for use on gears or roller bearings is formed of cup grease 50 lbs., Pb dust 1 lb., babbit dust 4 oz., and powdered white lead.

Electrical insulating composition. F. J. GROTEN, JR. U. S. 1,455,200, May 15. An impregnating compn. m. about 60° is formed of an oil such as China wood oil mixed with resinous polymers of *p*-coumarone, paraindene and other coal-tar hydrocarbon distillate components.

Electrical insulating composition. T. C. PROUTY. U. S. 1,453,726, May 1. A compn. adapted for manuf. of insulating slabs, switchboards, etc., is prepd. by mixing dry powdered talc with a phenolic condensation product or other temporary binder free from H<sub>2</sub>O and heating the mixt. to about 1100°. Oxides of Fe or Cr may be used with the talc.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

Philadelphia water supply, present and proposed. G. W. FULLER. *J. Am. Water Works Assoc.* 10, 347-64(1923).—The present supply is inadequate. Although filtered and treated with Cl<sub>2</sub> trade wastes frequently render it objectionable. Temporary help will be gained by intercepting sewers to cut out such wastes, and the extension of



the meter system. New supplies may be obtained from adjacent water sheds through storage reservoirs. The possibility of a ground water supply is not good.

D. K. FRENCH

**Water supplies in Calcutta and Madras.** STEWART. *Local Self-Govt. Gaz.* 8, 545-50(1922); *Pub. Health Eng. Absts.* May 12, 1923.—Colloidal matter in the filtered water of Calcutta indicated insufficient alum to produce coagulation, clarification, etc. The efficiency of the slow sand filter may have been reduced and the bacterial quality deteriorated. The Madras supply was also troubled with algae, and filtration through slow sand filters without previous treatment gave unsatisfactory results.

G. C. BAKER

**Progress report of the Committee on Industrial Wastes in Relation to Water Supply.** A. L. FALES, et al. *J. Am. Water Works Assoc.* 10, 415-30(1923).—Detrital material is classified as suspended or colloidal, dissolved mineral, vegetable and animal org., taste- and odor-producing and growth-producing substances, harmful bacteria, and poisons. Many types of mfg. wastes are discussed in detail and the soln. of the various problems should be treatment of the polluted water, treatment of the wastes before discharge, or elimination of the waste itself. A tentative bibliography is given.

D. K. FRENCH

**Methods of drinking-water examination.** W. OLSZŃSKI. *Chem.-Ztg.* 47, 273 (1923).—Volumetric estn. of sulfate by the benzidine method is advised. For the detection of Mn the use of 300 cc. of water is recommended. The same sample is used for the detn. of  $\text{NH}_3$ . After treating with  $\text{NaHCO}_3$  the sample is allowed to stand several hrs. and 200 cc. of the supernatant liquid poured off for the  $\text{NH}_3$  detn. The remainder is thoroughly shaken, and filtered, and the residue treated with benzidine acetate soln. and dild. to 300 cc. A blue color shows the presence of Mn. Iron salts do not interfere. The following procedure is given for the prepn. of the benzidine acetate soln.: grind 20 g. benzidine with 20 cc.  $\text{H}_2\text{O}$ , transfer to a 1-l. measuring flask and add about 750 cc.  $\text{H}_2\text{O}$ , add 50 cc.  $\text{AcOH}$  and dil. to the mark, shake, let stand for one day, and filter. The soln. should be kept in a dark flask. The test is sensitive to 1 part in 125,000,000. Qual. tests for Mn were also made with *o*-tolidine, but Fe oxidation products also produced a blue color. For the estn. of Mn the Marschall test (*Hyg. Waters* 1915) is recommended.

G. C. BAKER

**Zinc contamination in drinking water.** C. D. HOWARD. *J. Am. Water Works Assoc.* 10, 411-14(1923); cf. C. A. 17, 1680.—Zn from the corrosion of galvanized pipes is more frequently present in water than generally suspected. There are little data available as to its hygienic significance in small amts. The detn. of Zn should be made more frequently in water labs. A rapid method of estn. is given.

D. K. F.

**Pollution of drinking water by intestinal bacteria.** ERIK BONDO. *Nord. hyg. Tids.* 2, 13(1921); *Abstracts Bact.* 5, 512.—Lactose fermenters in drinking water were classified as belonging to warm-blooded or cold-blooded animals. Colorimetric  $p_{\text{H}}$  measurements, according to Clark and Lubs, were made. No differences in acid production with *B. coli* from warm-blooded or from cold-blooded animals were found but indole production was negative with the cold-blooded and positive with a majority of warm-blooded strains.

H. G.

**Hydrogen-ion concentration of natural waters in relation to disease.** W. R. G. ATKINS. *J. State Med.* 31, 223-6(1923).—Natural waters vary in reaction from about  $p_{\text{H}}$  5 for a bog pool to about  $p_{\text{H}}$  8.3 for a stream satd. with  $\text{Ca}(\text{HCO}_3)_2$ . Town supplies normally vary between  $p_{\text{H}}$  6.8 and  $p_{\text{H}}$  8. With the exception of bog waters, and those rich in metallic salts such as mine drainage waters, it seems that  $p_{\text{H}}$  values of natural waters are favorable for the existence of *Vibrio cholerae* and the typhoid bacilli group. In contrast to acid limits of Dernby and others the suggestion is made that water may be rendered safe for drinking by making it alk. as  $p_{\text{H}}$  10.5 by adding ash derived from vegetable matter, which is rich in  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ . The necessity of stating temps. when limiting and optimal values are given for the growth of various organisms is noted.

G. C. BAKER

**Interior treatment of boiler feed water.** A. J. LOPPIN. *Power* 57, 520-2(1923).—An outline of current practice.

D. B. DILL

**Progress report of Committee on Practicable Loadings for Purification Processes.** E. E. WALL, et al. *J. Am. Water Works Assoc.* 10, 494-503(1923).—Tentative conclusions for filter plant control are drawn up, but aside from setting a standard for a safe water it is felt that each community must set its own standard for color, hardness, taste, odor, etc. Any general conclusions formulated now would be premature and possibly misleading.

D. K. FRENCH

**The depth and grading of percolating filters.** W. J. READ. *Water & Water Eng.*

25, 133-4(1923).—There are three views concerning the way in which material should be placed in a filter: (1) The surface area should be as large as possible, *i. e.*, the filter should be shallow, down to a minimum of about 2 ft. 6 in.; (2) the purification is governed by the cu. capacity and is unaltered by the arrangement; (3) the most satisfactory depth of a filter is about 10 ft. or more. A filter of this depth is capable of purifying a greater vol. per ft.<sup>3</sup> than a shallow one. Data supporting the above views are included in the article.

H. D. CARTER

**Sanitation on Atlantic transports.** J. D. R. WOODWORTH. *Military Surgeon* 52, 290-9(1923); *Pub. Health Eng. Absts.* May 19, 1923.—Measures carried out on American transports at the Brooklyn, N. Y., ports are described.

G. C. BAKER

**Comprehensive review of the work on disinfection and sterilization by means of chemicals during the years 1913-1920.** H. F. KERSTEN. *Desinfektion* 7, 65-80.

H. G.

**Tastes and odors.** ALLEN HAZEN. *J. Am. Water Works Assoc.* 10, 506-7(1923).—No attention has been given to the effect of oxidizing action and biol. growth in the filtering process, especially slow sand filters. The free and albuminoid NH<sub>3</sub> detns. are felt to be a valuable index of certain kinds of odor-producing substances.

D. K. FRENCH

Filter for water (U. S. pat. 1,455,505) 1.

**Annales des services techniques d'hygiène de la Ville de Paris. Tome III. Compte rendu des travaux en 1921.** Paris: Gauthier-Villars & Cie. 342 pp. Reviewed in *Recherches et inventions* 4, 343(1923).

**JACKSON, PERCY G.: Boiler Feed Water.** 2nd Ed. revised and enlarged. London: Chas. Griffin & Co., Ltd. 143 pp. 5s. net. Reviewed in *Analyst* 48, 199(1923).

**Purifying water.** A. C. SPENCER. U. S. 1,455,363, May 15. A filter bed of greensand is used for purification of H<sub>2</sub>O and is revived when required by treatment with a soln. of NaCl followed by washing.

**Aeration of sewage.** T. H. FAIRBROTHER and A. RENSHAW. U. S. 1,455,435, May 15. In tank aeration of sewage, the latter is treated with an oxazine coloring material, *e. g.*, Meldola blue, with or without auramine O, in order to destroy protozoa without injury to useful bacteria.

**Filter bed for sewage disposal.** W. T. BURTIS. U. S. 1,454,723, May 8. Structural features.

**Apparatus for generating hydrocyanic acid for use in fumigating.** K. F. COOPER. U. S. 1,454,154, May 8.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

**The soils of Lubok Tamang and Cameron's Highlands.** V. R. GREENSTREET. *Malayan Agr. J.* 10, 231-3(1923).—Some analyses are included.

E. J. C.

**Examination of soil gases.** F. J. WARTH. *Agr. Res. Inst. Pusa Sci. Repts.* 1920-1, 24-5.—A table shows (by month) the variation of CO<sub>2</sub> in the soil gas.

H. W. EASTERWOOD

**Soil biology.** J. H. WALTON. *Agr. Res. Inst. Pusa Sci. Repts.* 1920-1, 28-9.—The loss of N from cattle dung during storage was small, while the loss from urine under aerobic conditions was 85% and under anaerobic conditions 15%. Expts. on composting phosphate rock with cake or green manure show some solubilization of the phosphate. Expts. on nitrification of mahua cake showed that the addition of fresh cake lowered the % of nitrate N in the soil to zero. This effect persisted 4 weeks. By composting with phosphate rock and S for 4 weeks resulted in 25% of the N of the cake becoming nitrifiable.

H. W. EASTERWOOD

**A new method of mechanical analyses of soils.** D. S. JENNINGS, M. D. THOMAS and WILLARD GARDNER. *Soil Science* 14, 485-99(1922).—A dil. deflocculated soil suspension is placed in a cylindrical vessel, kept in an upright position, and the concn. detd. as it changes with time at measured distances below the surface. Samples for analysis are drawn off at desired intervals by means of a multiple in-take pipet with openings turned horizontally. From the changes in density with time the relative amts. of particles of different sizes can be calcd. The method is proposed for making routine mech. analyses.

R. BRADFELD

**Microbiological analysis of soil as an index of soil fertility. II. Methods of the study of numbers of microorganisms in the soil.** S. A. WAKSMAN. *Soil Science* 14, 283-98(1922); cf. C. A. 17, 1856.—A representative composite sample of soil is dild. with 10-20 times its wt. of  $H_2O$  and shaken for at least 5 min. to get all organisms in suspension. The next dild. should be 1:10 or 1:100. The final dild. should be such as to give 40-200 colonies per plate. Sterile tap water was found best for making the dilds. A medium of standard compn. contg. no peptone, meat ext., soil ext. or similar substance which is variable in compn. should be used. Asparagine, purified casein or powdered egg albumin are to be preferred as sources of N. The final reaction should be about  $pH$  6.5. At least 6-10 plates should be used in plating out each sample, the plates then incubated at  $25^\circ$  for at least 7 days. The probable error or counts should not be greater than 3%. **III. Influence of fertilization upon numbers of microorganisms in the soil.** *Ibid* 321-46.—In a sandy loam not very rich in org. matter  $K_2O$  and  $P_2O_5$  stimulated the growth of organisms more in the presence of lime; lime caused decrease in the numbers of fungi;  $NaNO_3$  stimulated bacteria and actinomycetes but not fungi;  $(NH_4)_2SO_4$  stimulated fungi and retarded bacteria because of the high acidity developed. When  $CaO$  was used with  $(NH_4)_2SO_4$  bacterial growth was stimulated as much as with  $NaNO_3$ . Manure stimulated strongly all organisms developing on the plates. Crop production ran nearly parallel with bacterial numbers.

RICHARD BRADFELD

**The influence of worms on the condition and productivity of soils.** R. HEYMONS. *Z. Pflanzenernähr. Düngung (A)* 2, 97-129(1923).—In general, worms increase yields. This is due partly to such chem. effects as increased N content and partly to phys. effects. Some chem. data are included. W. H. FRY

**Modifications of the soil flora induced by applications of crude petroleum.** I. L. BALDWIN. *Soil Science* 14, 465-75(1922).—Most types of bacteria were inhibited by applications of crude petroleum, ranging from 0 to 200 cc. per 2 gal. pot; others were markedly stimulated so that the total no. was increased.  $NH_3$  and  $NO_3$  production were both retarded at first but showed a slight recovery later. Crop growth was not injured by the smaller applications. The crude petroleum after incorporation in the soil is gradually broken down into simpler non-toxic products. R. BRADFELD

**Chemical studies in conjunction with field tests of soils and fertilizers.** H. P. STUCKEY. Georgia Agr. Expt. Sta., 35th Ann. Rept. 8-9(1922).—S in a compost, used at the rate of 2%, prevented the loss of N from a mixt. of cottonseed meal, rock phosphate, soil and manure. A similar compost without S lost 50 to 70% N.

J. J. SKINNER

**Crops and soils.** H. P. STUCKEY. Georgia Agr. Expt. Sta., 35th Ann. Rept. 8(1922).— $CaSO_4$  applied to soil growing alfalfa produced no increase.  $H_2SO_4$  used at the rate of 50 lb. per acre increased yield, which was probably due to the action of the acid on the soil, rather than to an increase in the amt. of S. J. J. SKINNER

**Relation of soil nitrogen, nitrification and ammonification to pot experiments.** G. S. FRAPS. Texas Agr. Expt. Sta., Bull. 283, 5-51(1921).—The av. wt. of N removed by 4 crops increases with the % total N in the soil. The first crop is much larger than the succeeding crops. Crops of nearly the same wt. of dry matter may vary considerably in N content. The 4 crops usually remove 6-9% of the total N of the soil. On an av., the N of surface soils is better taken up than that of subsoils. On an av., non-acid soils give up more N to crops than acid soils. Little relation could be found between the N taken up by the soil and the active  $P_2O_5$  of the soil, or the acid consumed, or the  $CaO$ . There is a close relation between the amt. of N removed by the first crop and the amt. of available nitric N. There is a discussion of the correlation between the N content of the soil and that taken up by the 4 crops as estimated by statistical methods. W. H. FRY

**The relation of soil moisture to physiological salt balance for plants.** J. W. SHIVE. *Soil Science* 14, 391-411(1922).—Buckwheat was grown in soil cultures receiving 21 different sets of salt proportions of  $KH_2PO_4$ ,  $Ca(NO_3)_2$  and  $MgSO_4$  in 3 different series in which the moisture content was maintained at 30, 60 and 90%, resp. of the max. water-retaining capacity of the soil. 60%  $H_2O$  was considered optimum. The balance of salt proportions giving high yields was not materially altered by variations in the degree of soil moisture when the total osmotic concns. were kept const. Pronounced shifting of the balance occurred only with marked variations in the total concn. of the solns. added. Yield differences resulting from variations in soil  $H_2O$  content were as pronounced as those resulting from variations in salt proportions. High yields from cultures with medium soil  $H_2O$  (60%  $H_2O$ -holding capacity) were always greatly superior to the corresponding yields from cultures with either higher or lower  $H_2O$  content.

Hence the max. plant-producing value of any fertilizer mixt. can only be attained with optimum  $H_2O$  conditions.

R. BRADFIELD

**Relation between heat of wetting, moisture equivalent and unfree water.** G. J. BOUYOUCOS. *Soil Science* 14, 431-4(1922).—A close and consistent relationship was found between the heat of wetting and the unfree water but no such relationship was found with the moisture equiv. The moisture equiv. of highly colloidal soils was abnormally high.

R. BRADFIELD

**The manganese content of some Dutch soils and sub-soils.** D. H. WESTER. *Pharm. Weekblad* 60, 446-51(1923).—The Mn content of cultivated soils varied between 6.2 and 120 mg. per 100 g. of dry soil, the fertile soils contg. more Mn than the infertile. No const. relation was found between the Mn and Fe content. The ash of the corolla and seeds of plants generally showed a higher % of Mn than the soil in which the plants were grown. In *Digitalis purpurea* no relation was found between the Mn content of the leaves and that of the soil. Some of the sub-soils contained only traces of Mn.

A. W. DOX

**Sulfur oxidation in inoculated and uninoculated greensand mixtures and its relation to the availability of potassium.** W. RUDOLFS. *Soil Science* 14, 307-19(1922).—Greensand contg. 4.53%  $K_2O$ , 1.16%  $P_2O_5$ , and 1.08%  $SO_3$  was composted with sulfur and soils in varying proportions with additions of  $(NH_4)_2SO_4$ . From 3 to 5% of the total  $K_2O$  was liberated when the  $pH$  values were reduced to 2.7-2.3. Two parts S were required to liberate 1 part  $K_2O$ ; therefore, about 1 part S to 10 parts of greensand is sufficient. Soy beans made as good growth in quartz sand with Shive's nutrient soln. in which the K was supplied by composted greensand as when it was supplied by the usual K salts.

RICHARD BRADFIELD

**Acid phosphate production by the Lipman process. I. Effects of moisture content of sulfur-floats-soil mixtures on sulfur oxidation activities.** J. S. JOFFE. *Soil Science* 14, 479-83(1922).—Previous work indicated that 50-60% satn. was optimum for the S-oxidizing organism.  $H_2O$  has commonly been added in quantities just sufficient to replace that lost by evapn. Such a procedure makes no provisions for the  $H_2O$  rendered unavailable to the organism by the reactions: (1)  $2S + 2H_2O + 3O_2 = 2H_2SO_4$ , (2)  $Ca_3(PO_4)_2 + H_2SO_4 + 2H_2O = Ca_2H_2(PO_4)_2 + CaSO_4 \cdot 2H_2O$ , (3)  $Ca_2H_2(PO_4)_2 + H_2SO_4 + 2H_2O = CaH_4(PO_4)_2 + CaSO_4 \cdot 2H_2O$ . Results indicate that the initial  $H_2O$  content should be about 50% of satn. and as the reactions proceed it should be gradually raised to 60%; 75% was detrimental.

R. BRADFIELD

**The effect of nodule bacteria on the yield and nitrogen content of canning peas.** F. B. FRED AND O. C. BRYAN. *Soil Science* 14, 413-6(1922).—Inoculation increased the yield of tops and roots of canning peas 179 lbs. per acre, hulls 51.5 lbs. per acre and total N fixed 13.2 lbs. per acre under normal field conditions. The yield of seed was not affected but the N content of the seed was increased. These figures are probably low owing to the presence of a few nodules on the uninoculated peas.

R. B.

**The destruction of fat in soil.** MAX RUBNER. *Arch. Hyg.* 91, 290(1922).—In 1887 different fats were mixed with soils that were kept moist and after various periods the amt. of decompn. was detd. After 1 yr. 22.9% of butter fat was destroyed, 9.9% of cod-liver oil, and 9.7% of oleic acid. After 12 yrs. 70% of the cod-liver oil and 38.1% of the butter fat were destroyed. During the last 23 yrs. the soils were not kept moist and it was found that the dryness caused decompn. to stop, probably because of the accumulation of fatty acids which are usually washed out in soil by moisture.

JULIAN H. LEWIS

**Adsorption of plant food by colloidal silica.** R. C. WILEY AND N. E. GORDON. *Soil Science* 14, 441-8(1922).—The metals in general, and the  $NO_3$  and  $SO_4$  radicals were negatively adsorbed by both the hydrogel and hydrosol of silica. The  $PO_4$  radical was adsorbed positively by the hydrogel and negatively by the hydrosol. The adsorbed  $PO_4$  could be washed out only with extreme difficulty. No basic salts were used in this study.

R. BRADFIELD

**Influence of hydrogen-ion concentration on the adsorption of plant food by soil colloids.** E. B. STARKKEY AND NEIL E. GORDON. *Soil Science* 14, 449-57(1922).—In a continuation of work previously reported (*C. A.* 17, 1102) the adsorption of cations by silica gel was found to be increased at higher  $pH$  values; the adsorption of  $PO_4$  ions was in some cases decreased while the  $NO_3$  and  $SO_4$  ions were not markedly affected.  $Fe(OH)_3$  gel was a much better adsorbent for the salts studied than that of silica.

R. BRADFIELD

**Nitrate accumulation under straw mulch.** W. A. ALBRECHT. *Soil Science* 14, 299-305(1922).—Under straw-mulched, fallow soil for 3 yrs. nitrate N failed to accumulate beyond 27 lbs. of nitrate N per 2,000,000 lbs. of soil, as compared with over 200

lbs. without mulching. The  $H_2O$  and  $NO_3$  content showed general reciprocal relations during this time, suggesting a direct or indirect relationship. The mulched plot has an av. temp.  $10^\circ$  lower than those unmulched during the months of June to August, suggesting possible correlation with  $H_2O$  and  $NO_3$  production. The study indicates that mulching with straw is a practice to be used with discretion. W. A. ALBRECHT

**Basic slags as sources of lime.** F. E. BEAR AND J. L. GAYLE. Ohio Agr. Expt. Sta., *Mo. Bull.* 7, 103-4 (1922).—Expts. with lettuce indicated that Thomas slag and Duplex slag had a neutralizing value equal to about 50% that of limestone. When used in equiv. amts. they produced about equal influence on the nitrification of  $(NH_4)_2SO_4$  when added to an acid soil. M. S. ANDERSON

**Effect of cultivation during the growing season on moisture content and formation of nitrates in the soil.** W. H. SACHS AND R. H. AUSTIN. Arkansas Agr. Expt. Sta., *Bull.* 81, 41-2 (1922).—Expts. made in connection with the regular cultivation of corn indicated that deep cultivation gave the highest seasonal av. of  $NO_3$ . The growth of weeds resulted in a heavy drain on both  $NO_3$  and  $H_2O$ . In July non-cropped plots free from weeds showed 100 lbs. nitrate N per surface acre as compared with 2 lbs. per acre in the presence of weeds. Attention is called to the possible value of any crop, even weeds, as a means of retaining the sol. N produced. M. S. ANDERSON

**The German nitrogen industry and its importance to agriculture and human nutrition.** F. HONCAMP. *Z. Pflanzenernähr. Düngung (B)* 2, 147-62 (1923).—General. W. H. FRY

**The effect of available nitrogen on the protein content and yield of wheat.** R. E. NEIDIG AND R. S. SNYDER. Univ. Idaho Agr. Expt. Sta., *Research Bull.* No. 1, 56 pp. (1922).—Marquis and Palouse Bluestem wheats were grown in the greenhouse on soils and soil-sand mixts. contg. different amts. of available N, and on soils to which varying amts. of N were added in the form of  $NaNO_3$ ,  $(NH_4)_2SO_4$ , hydrolyzed wheat ext., casein, and keratin. These forms of N produced in Marquis wheat a marked increase in the protein content and yield. With the Palouse Bluestem variety, where the amts. of available N added were less than in the preceding expt., there was an increase in yield, but not in protein content. N in the form of casein and keratin gave a greater increase in yield and protein content than any other form of available N. Cumulative addns. of  $NaNO_3$  throughout the growing period gave a higher yield and protein content in all soil-sand mixts. than was obtained when the same amt. of  $NaNO_3$  was added at the time of planting. Field series showed that when there was a sufficient amt. of available N present in the soil to insure the max. plant growth during the early period a high yield was obtained; but when the N was sufficient to insure an available supply during the entire life cycle both yield and protein content were increased under the climatic conditions prevailing. Under field conditions available N will show the greatest effect on protein content and yield when the climatic factors are most favorable. Both climate and available N play an important role. The effect of the former factor is chiefly in its influence on the nutrition of the plant. Given an ample supply of available N in the soil, it seems that moisture is the chief climatic factor affecting yield and protein content. P. R. DAWSON

**Water-insoluble nitrogen in calcium cyanamide.** HEINRICH PINCASS. *Chem.-Ztg.* 47, 253-4 (1923).—In the manuf. of  $CaCN_2$ , several factors were studied which included variations in the compn. of the mixt.; variations in temp.; the effect of certain impurities upon the total N content of the cyanamide formed and the amt. of insol. N. Temps. of  $900^\circ$ ,  $1,000^\circ$  and  $1,100^\circ$  used on the same mixt. showed that the later temp. was necessary for a satisfactory fixation of N. The total N content obtained at  $900^\circ$  was 0.65 and at  $1,100^\circ$ , 13.5%. Insol. N obtained at  $900^\circ$  was 0.33% and at  $1,100^\circ$ , 1.8%. A large amt. of  $CaC_2$  and a small amt. of  $SiO_2$  tended to give a low content of insol. N while larger amts. of N were fixed when 4-6%  $SiO_2$  was present. M. S. ANDERSON

**End liquor lime.** NOLTE. *Mitt. deut. Landw.-ges.* 38, 100 (1923).—Practically the entire fertilizing value of end liquor lime from potash works lies in its content of  $CaO$ , about 40%. A portion of this is, however, present as  $CaCl_2$ . Ground limestone and lime are preferable to end liquor lime. K. D. JACOB

**Fertilizing with gas water.** TH. REMY AND F. WEISKE. *Mitt. deut. Landw.-ges.* 38, 106-8 (1923).—Because of its relatively high content of thiocyanates, cyanides, and free  $NH_3$ , gas water may injure plants when used as a top-dressing. The injury is less marked if the gas water is dild. or if cool weather and heavy rainfall prevail at the time of its application. When used as a top-dressing the injurious effects of the gas water are most noticeable during the first few weeks, later being offset largely by the utilization of the N. When worked into the soil gas water approximates  $(NH_4)_2SO_4$

in its action. To prevent loss of N the gas water may be treated by any of the methods used for concd. liquid manure. A number of plot expts. with gas water are described and discussed. K. D. JACOB

**Pulverized ferrous sulfate as a fertilizer and plant disinfectant.** LOBBECKE. *Mitt. deut. Landw.-ges.* 36, 186(1923).—The application of pulverized, 60%  $\text{FeSO}_4$  at the rate of 600 lbs. per hectare increased the yield of sugar beets by 11% and the total raw sugar by 15%. The plants on the plots receiving  $\text{FeSO}_4$  were practically free from wire worms while the check plots were badly infected. K. D. JACOB

**Silica and silicates in relation to plant growth and composition.** C. J. SCHOLLENBERGER. *Soil Science* 14, 347-62(1922).—Data from two crops of soy beans, and one each of oats and buckwheat, indicate that  $\text{SiO}_2$  added as air-dry hydrated  $\text{SiO}_2$  + dialyzed  $\text{SiO}_2$ , blast furnace slag,  $\text{CaSiO}_3$ , and water glass increased in the availability of the  $\text{SiO}_2$  in the order named. Buckwheat showed the smallest difference in  $\text{SiO}_2$  content, oats the largest.  $\text{CaCO}_3$  seemed to decrease the amt. of  $\text{SiO}_2$  taken up. Ground furnace slag was an effective source of bases and its  $\text{SiO}_2$  was slightly available but there was no evidence that it enabled the plant to utilize more  $\text{P}_2\text{O}_5$  from rock phosphate; with soy beans the basic silicates seemed to increase the  $\text{P}_2\text{O}_5$  content more than the corresponding carbonates. This was not true of the wheat crop. R. BRADFIELD

**Sulfur as a fertilizer for cotton.** E. B. REYNOLDS AND A. H. LEIDIGH. *Soil Science* 14, 435-40(1922).—Applications of S as high as 1000 lbs. per acre increased the yield of cotton in 1920. In 1921 larger applications were used and the best results were obtained where lime was used with the S. The beneficial effect was considered due to the neutralization of the high acidity produced by the oxidation of the large quantities of S. Cotton root-rot was neither prevented nor controlled by any S application. R. BRADFIELD

**Sulfur as an important fertility element.** C. O. SWANSON AND W. L. LATSHAW. *Soil Science* 14, 421-30(1922).—Analyses of 96 Kansas soils, distributed throughout the state, show that cropping has resulted in a distinct lowering of the S content when compared with the virgin sod in the humid sections of the state. The loss of S is greater than the loss of P and is proportionate to the loss of N. The analyses indicate that S may become a limiting factor in crop production. In the semi-arid regions of the state the loss of S was small. R. BRADFIELD

**Blue sprays and blue vines.** ARTHUR CADORET. *Prog. agr. vit.* 79, 380-2(1923).—A summary of the advantages of a basic Bordeaux mixt. (blue), contg. equal parts of lime and  $\text{CuSO}_4$ , with recommendations as to its application. P. R. D.

**Potassium permanganate as a treatment for vine diseases.** G. RUBAN. *Rev. vit.* 53, 269-72(1923).—A discussion of the advantages and disadvantages of  $\text{KMnO}_4$  as an insecticide and fungicide, and the conditions to which it is adapted. P. R. D.

**Coöperative experiments with copper carbonate dust and other substances for smut control.** W. P. FRASER AND P. M. SIMMONDS. *Sci. Agr.* 3, 297-302(1923).

J. J. S.  
Experiments on the dust method of smut control. A. KELSALL. *Sci. Agr.* 3, 303-7(1923). J. J. S.

**Action of insoluble oxides upon potato mildew (*Phytophthora infestans*).** G. VILLEDIEU AND MAE. G. VILLEDIEU. *Compt. rend.* 176, 534-6(1923).—In the hanging drop, conidia of *P. infestans* suffered no inhibition of germination or development in a medium consisting of the filtrate from 24 hrs. contact of distd.  $\text{H}_2\text{O}$  and any one of the following:  $\text{MgO}$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{CdO}$ ,  $\text{Ni}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{CuO}$ , and  $\text{Hg}_2\text{O}$ . However, such development was nearly or completely inhibited by contact with these compds. in the finely divided, solid condition. This toxicity is due, in part at least, to the basic function of the oxides concerned;  $\text{Bi}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Pb}_2\text{O}_3$ , and  $\text{MnO}_2$  proved non-toxic under the same conditions. P. R. DAWSON

**Control of lettuce drop by the use of formaldehyde.** W. S. KROUT. *J. Agr. Research* 23, 645-54(1923).—From 15 to 20 mins. were required to kill sclerotia in both 1 to 50 and 1 to 100 solns. of  $\text{HCHO}$ . Mycelium were also killed in solns. of the 2 strengths of  $\text{HCHO}$  in equal periods. In most cases 1-100  $\text{HCHO}$  soln. killed sclerotia and mycelium 20" below the soil surface. A 4 years' test demonstrated that 1-100  $\text{HCHO}$  soln. is an effective fungicide when used to control *Sclerotinia liberiana* in greenhouse soils. P. C. COOK

**Insecticidal use of chloropicrin.** RYO YAMAMOTO. *Rikugakyo Kenkyujo Thô 1*, 1-8(1922).—By spraying  $\text{CCl}_3\text{NO}_2$  into a storehouse used for rice, wheat, etc., noxious insects are killed without bad effects on the goods. Generally about 0.225-0.35 g. per cu. shaku is an effective quantity. The active period is 48-70 hrs. and the higher the

temp. the more effective this substance is. Exptl. results performed on a large scale are given. The reagent is also applicable for killing of pupas in cocoons. K. K.

Insecticide pyrethrum, preparations from it, and its activity. J. CHEVALIER. *Rev. vit.* 58, 320-2(1923). P. R. D.

Determination of HCHO in the presence of  $\text{CuSO}_4$  (JAKES) 7. Relation of H-ion concentration to flocculation of a colloidal clay (BRADFELD) 2. Oxidation of zinc sulfide by microorganisms (RUDOLFS, HELBRONNER) 11C.

ANDRÉ, G.: Propriétés générales des sols en agriculture. Paris: Armand Colin. 184 pp. Bound Fr. 6; paper Fr. 5. Reviewed in *Recherches et inventions* 4, 272(1923); *Bull. soc. ind. Mulhouse* 89, 184(1923).

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

The problem on provisions. UMETARO SUZUKI. *Rikugaku Kenkyujo Ito* 1, 38-45(1922).—To conserve rice S. has attempted successfully to manuf. saké by fermenting potato starch contg. 0.1% amino acids (alanine, leucine, tyrosine, etc.), to which pure alc. is added until its content becomes about 18%.  $\text{CCl}_3\text{NO}_2$  is a good insecticide for use with stored rice. Production of alc. is also discussed. K. K.

Denatured alcohol in Canada. I. R. E. GILMORE. *Can. Chem. Met.* 7, 116-8 (1923).—A "summary of the compu., use and consumption of denatured alc., with a review of regulations in the U. S. and Gt. Britain." E. J. C.

Preparation of vinegar from fruits by the Boerhave process. H. WÜSTENFELD. *Deut. Essigind.* 26, 215-6, 227-9(1922).—The old Dutch process of Boerhave is modified by using the skins as the packing and bacteria carrier in the generators in place of shavings. The acclifying barrels are flooded with "stock" and completely drawn off periodically to introduce the necessary air into the interstices. H. A. LEPPER

Direct production of vinegar from beets by the Boerhave process. H. WÜSTENFELD. *Deut. Essigind.* 27, 31-3(1923).—This process (preceding abstr.) can be used in making vinegar from sugar beets. H. A. LEPPER

Treating molasses (U. S. pat. 1,449,134) 28.

DUJARDIN, J., DUJARDIN, LUCIEN, and DUJARDIN, RENÉ: Notice sur les instruments de précision appliqués à l'œnologie, à la pomologie et à la brasserie. Paris: J., L., and R. Dujardin. 6th ed., nearly 300 pp. Reviewed in *Ann. fals.* 16, 113 (1923).

Alcohol from galactose. E. C. SHERRARD. U. S. 1,454,521, May 8. An aq. soln. of galactose is partially neutralized with lime or  $\text{CaCO}_3$  until not more than 50 cc. of 0.1 N NaOH is required to neutralize 100 cc. of a test sample. The soln. is evapd. to a content of 6-10% total reducing sugar, mixed with a soln. of autolyzed yeast, sterilized and fermented with yeast at a temp. of about 27-32° to produce alc. If acidity tends to rise during the fermentation, an antacid is added to maintain it at about 50° as specified. The process may be used without any royalty payment.

Beverage of low alcohol content. H. HEUSER. U. S. 1,455,397, May 15. The flavor of dealcoholized beverages is improved by a secondary yeast propagation in the beverage after addn. of a nitrogenous yeast food such as aspartic acid or products of autolysis of yeast.

Yeast. F. HAYDUCK. U. S. 1,449,102, Mar. 20. In the aeration method of yeast production, the yeast growth is carried out in a nutrient soln. consisting essentially of sugar material, e. g., raw or refined beet sugar, and yeast-nourishing inorg. salts, which may include  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , and  $\text{CaSO}_4$ , in amts. sufficient to supply all essential yeast foods during the period of yeast propagation. The initial diln. of the nutrient soln., e. g., not more than 2° Balling, is sufficiently low that the salts are innocuous to the yeast.

Yeast. F. HAYDUCK. U. S. 1,449,103, Mar. 20. In production of yeast from nutrient solns. (such as those of the general type referred to in the preceding pat.) in which the inorg. salts present tend to cause development of undue acidity during the period of yeast propagation, deleterious excess acidity is neutralized, e. g., by a carbonate.

A compd. such as  $(\text{NH}_4)_2\text{CO}_3$  may be used which serves the purpose of a neutralizing agent and also supplies some yeast-assimilable N to assist in the yeast growth.

**Yeast.** F. HAYDUCK. U. S. 1,449,104, Mar. 20. Yeast is grown by a process somewhat similar to that of U. S. 1,449,102 except that Na salts such as sulfate, phosphate or carbonate may be used in prep. the nutrient solns. instead of K salts. The nutrient soln. may, *e. g.*, contain sugar 100,  $(\text{NH}_4)_2\text{SO}_4$  4.5,  $\text{NH}_4\text{H}_2\text{PO}_4$  1.5,  $\text{Na}_2\text{SO}_4$  3,  $\text{MgSO}_4$  0.5 and  $\text{H}_2\text{O}$  5000 parts.  $\text{CaCO}_3$  may be added as a neutralizing agent. Yeast propagated in nutrients of this type (so that Na largely replaces K in the cell compn. of the yeast) is of generally good quality and "sodium yeasts" so cultivated through many generations have good baking characteristics.

**Yeast.** F. HAYDUCK. U. S. 1,449,105, Mar. 20. Propagation of yeast is initiated in a dil. soln. contg. all essential yeast nutrient substances and during the period of yeast propagation there is continuously added a soln. of all essential yeast nutrient substances. The latter soln. may have a higher concn. than that in which the propagation is initiated, *e. g.*, 12° Balling as compared to 1°. Relatively large yields of yeast with but very little production of alc. are obtained, and the soln. may be aerated during, and for a time subsequent to, the addition of the nutrient soln. U. S. 1,449,106 relates to generally similar processes, with special application of the method to nutrient solns. formed from sugar (or molasses) and inorg. nutrient salts. Acidity developed during the yeast propagation is preferably neutralized, in part at least.

**Continuous yeast propagation.** F. HAYDUCK. U. S. 1,449,107, Mar. 20. Seed yeast is suspended in a relatively small depth of nutrient soln.,  $\text{H}_2\text{O}$  or other suitable liquid, in a comparatively deep vat, the liquid is aerated and nutrient soln. is added, preferably continuously and in more concd. form. As soon as a sufficient amt. of propagating liquid has thus accumulated, yeast-contg. soln. is withdrawn and may be led to separators at substantially the same rate that fresh nutrient soln. is supplied to the vat.

**Continuous yeast propagation.** F. HAYDUCK. U. S. 1,449,108, Mar. 20. A non-toxic aq. liquid, which may be  $\text{H}_2\text{O}$  or a dil. yeast-nutrient soln., is mixed with seed yeast which may be added in a quantity approximating that which can be grown in the portion of the nutrient soln. originally taken. During the yeast propagation, nutrient soln. may be continuously added and soln. carrying yeast simultaneously continuously withdrawn at the same rate. Liquid sepd. from the withdrawn yeast may be used in part for replenishing the contents of the propagating vat and antacid substances may be added during the process to prevent development of deleterious acidity. The process is adapted for use with solns. of sugar (or molasses) employed with inorg. salts as yeast nutrient materials.

**Yeast.** F. HAYDUCK. U. S. 1,449,109, Mar. 20. During yeast propagation in solns. in which a deleterious acidity tends to develop, a substance, *e. g.*,  $\text{NH}_4\text{OH}$ , is added which serves to neutralize excess acidity and supply yeast-assimilable N. This neutralizing agent may be mixed with the relatively concd. nutrient solns. added as described in U. S. 1,449,105-6.

**Yeast.** F. HAYDUCK. U. S. 1,449,110, Mar. 20. Alk. nutrient solns., *e. g.*, a soln. formed of molasses 100,  $\text{NH}_4\text{OH}$  equiv. to N 2, superphosphate equiv. to phosphoric acid 2,  $(\text{NH}_4)_2\text{SO}_4$  0.5 and  $\text{H}_2\text{O}$  500 parts, may be used for yeast propagation by allowing the soln. gradually to run into a more dil. aq. liquid in which seed yeast is suspended. The yeast is enabled to assimilate the free alkali by this method, without injury by an excess accumulation of alkali at any one time. The free alkali also precludes injurious effects from acids which otherwise might form and accumulate.

**Yeast.** F. HAYDUCK. U. S. 1,449,111, Mar. 20. In the propagation of yeast in nutrient solns. comprising sugar or molasses and inorg. yeast-nutrient salts (*e. g.*, sulfates), acid (*e. g.*,  $\text{H}_2\text{SO}_4$ ) is allowed to form and accumulate in the nutrient soln. to an extent sufficient to give the yeast adequate protection against infection and the yeast prepd. in the presence of this accumulated acid is then used as seed yeast for propagation in a soln. essentially formed from sugar or molasses and inorg. yeast-nutrient salts and during this main propagation excess acid formed is neutralized.

**Antiseptics in yeast propagation.** F. HAYDUCK. U. S. 1,449,112, Mar. 20. Antiseptics such as  $\text{CH}_3\text{O}$  or formic acid are added continuously to a vat in which yeast propagation is taking place, at such a slow rate that the antiseptic is assimilated by the yeast. If a relatively concd. portion of nutrient soln. is added to a relatively dil. portion, the antiseptic may be mixed with the concd. portion so as to assist in maintaining it free from infection.

**Settling yeast.** F. HAYDUCK. U. S. 1,449,113, Mar. 20. Settling of yeast is facilitated by rendering the liquid in which the yeast is suspended slightly alk., *e. g.*,



by adding NaOH. The sepd. yeast may advantageously be acidified before pressing to avoid infection.

**Yeast production from molasses.** M. NILSSON and N. S. HARRISON. U. S. 1,449,127, Mar. 20. A soln. formed essentially from molasses (preferably beet molasses) and  $\text{NH}_4$  phosphate or other inorg. compds. supplying yeast-assimilable N and P is used for commercial yeast production, with aeration, and excess acidity is neutralized during the period of yeast propagation.

**Freeing propionates from acetates.** J. M. SHERMAN and E. O. WHITTIER. U. S. 1,450,392, Apr. 3. Propionates are purified and freed from acetates by the action of bacteria which decompose acetates but have little or no effect on propionates, e. g., *Proteus vulgaris* or *Bacterium alcaligenes*. These organisms may be added to a propionic fermentation mixt. or may be used for purification of propionates contaminated with acetates, as a subsequent procedure following the principal fermentation process in which the mixed salts are produced.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**The cinchona (quinine) industry in Java.** W. N. SANDS. *Tropical Agriculturist* 59, 352-70(1922).—Several factors involved in the growth of cinchona and the extn. of quinine are discussed. An acre of cinchona trees in Java yields about 125 lbs. of dry bark in the first year of production and increases annually to about 630 lbs. in the 5th year. The first crop of bark yields about 5% quinine sulfate and the quinine content increases to about 8% in the 5th year.

**Experiments on sandalwood oil.** B. SANJIVA RAO, J. J. SUDBOROUGH AND H. E. WATSON. *J. Proc. Asiatic Soc. Bengal, Proc. 8th Indian Sci. Cong.* 17, 123(1922).—The soly. in 70%  $\text{EtOH}$  and the optical activity of the oil were compared after exposure to sunlight, diffused light and after keeping dark. Only by exposure to sunlight was the soly. diminished. Long boiling with  $\text{H}_2\text{O}$  changed the optical activity (cf. Briggs, C. A. 10, 1576) and decreased the soly. in  $\text{EtOH}$ , though the % alcs. did not change.  $\beta$ -Santalol was probably converted to  $\alpha$ -santalol.

**Determination of morphine and the secondary alkaloids in opium and its galenical preparations.** M. A. MANCINI. *Boll. chim. farm.* 62, 3-8, 35-9, 69-71, 101-5(1923).—From comparative studies of the various methods for the detn. of morphine M. considers that of the U. S. Pharmacopeia the best, and next in the order of preference the method of the French Codex and that of Tingle. For the detn. of the secondary alkaloids in opium and opium preps. the method of van der Wielen, modified by the substitution of  $\text{C}_6\text{H}_6$  for  $\text{Et}_2\text{O}$ , is the most satisfactory. Narcotine comprises about 75% of the secondary alkaloids. It is sol. in 12 parts of  $\text{C}_6\text{H}_6$  and in 178 parts of  $\text{Et}_2\text{O}$ , whereas the remaining alkaloids, papaverine, thebaine, codeine and narceine, are about equally sol. in  $\text{C}_6\text{H}_6$  and  $\text{Et}_2\text{O}$ . Hence  $\text{C}_6\text{H}_6$  gives a more complete extn. than  $\text{Et}_2\text{O}$ . The av. of 3 detns. by the modified method was 7.04%, by the original method 6.42%. Analysis of a known mixt. of morphine and the 5 secondary alkaloids in the proportions in which they occur in opium gave the theoretical value for the secondary alkaloids by the modified method.

**Identification of cocaine and its substitutes.** GERMAINE WALKAND. *J. pharm. Belg.* 4, 809-12, 893-9(1922); cf. C. A. 17, 1299.—Analytical methods applicable to the identification of the following are described: cocaine-HCl, acocine, nirvanine, eucaine, euphthalmine and tropacocaine.

**Impure phenacetin.** M. A. VANDERMEULEN. *J. pharm. Belg.* 5, 294(1922).—A sample of phenacetin answered to all of the requirements of the Belg. Pharmacopeia but gave the odor of petroleum ether on trituration. Neither pulverization nor heating at  $110^\circ$  will completely remove the solvent. Some other solvent should be used in crystallizing the product.

**Terpinol.** R. HUERRE. *Repert. pharm.* 35, 35-6(1923).—The French Pharmacopeia states that terpinol on heating at  $100^\circ$  loses 10% of its wt., which corresponds to 1 mol. of  $\text{H}_2\text{O}$  of crystn. H. finds the loss in wt. to depend entirely on the length of time of heating. This is due to sublimation of the terpinol, which takes place at temps. as low as  $60^\circ$ .

**Falsified ergot of rye.** GEORGES TANRET. *Repert. pharm.* 35, 69-71(1923).—There was recently found on the Parisian market a lot of ergot purporting to be of Spanish origin, which contained about 15 to 18% of grains differing noticeably from true

ergot. These grains were formed of dough prepd. from wheat flour and colored by dipping into red ink and then into a black iron-tannin ink. This method of falsification can readily be detected by rubbing the grains or immersing them in water, either of which removes the coloring material and exposes the white dough beneath.

A. G. DuMEZ.

**Conservation of solutions of certain medicaments.** LABAT. *Reper. pharm.* 35, 71(1923).—Benzoic acid is a very satisfactory preservative for solns. of certain alkaloids. Only 2 g. per l. is necessary for adrenaline solns. In this concn. the solns. can be tyndalized or sterilized by boiling without discoloration. For solns. of morphine, stovaine, syncline or novocaine, with or without adrenaline, 1 g. per l. is sufficient. Benzoic acid is also a more satisfactory preservative for hypodermic solns. than cherry laurel water or phenol because of its greater efficacy and because it is non-irritant.

A. G. DuMEZ.

**Veramon.** E. STARKENSTEIN. *Ber. pharm. Ges.* 33, 51-7(1923); cf. C. A. 17, 447.—Expts. are described tending to demonstrate that a new compd. is formed when dimethylaminophenylmethylpyrazolone and diethylbarbituric acid are melted together at definite temp., the new substance possessing a color differing from either of its components; that the 1st named component no longer yields its characteristic reactions; and that the new compd. is quant. split into its 2 components by HCl.

W. O. E.

**Veramon.** J. HERZOG. *Ber. pharm. Ges.* 33, 57-62(1923).—Controversial, with respect to the claims made by S. (see preceding abstr.)

W. O. E.

**A few data on some Dutch essential oils.** A. RECLAIRE. *Perfumery Essent. Oil Record* 14, 119b(1923).—Exptl. garden-grown plants yielded oils showing the following properties: rue  $d_{15}$  0.8513,  $\alpha_D$   $-0.4^\circ$ ,  $n_D^{20}$  1.4354, 3 vol. sol. in 70% alc.; lavender  $d_{15}$  0.8808-0.8850,  $\alpha_D$   $-7.2^\circ$ ,  $n$  1.4645-1.4648, 3-4.5 vol. sol. in 70% alc.; hyssop  $d_{15}$  0.9293,  $\alpha_D$   $-31.2^\circ$ ,  $n$  1.4888, 1 vol. sol. in 90% alc.; origanum  $d_{15}$  0.8858,  $\alpha_D$   $-13.2^\circ$ ,  $n$  1.4945, 23% phenols; thyme  $d_{15}$  0.9217,  $n$  1.4970, 1.6 vol. sol. in 80% alc., 35% phenols; fleabane  $d_{15}$  0.9173,  $\alpha_D$   $23.2^\circ$ ,  $n$  1.5203, cloudy soln. in 90% alc.; anthemis  $n$  1.4851; tansy  $d_{15}$  0.9252,  $\alpha_D$   $-15.5^\circ$ ,  $n$  1.4854, cloudy soln. 10 vol. in 70% alc.; wormwood  $d_{15}$  0.9627,  $n$  1.4939, 8 vol. sol. in 80% alc.

W. O. E.

**Pluchea lanceolata as adulterant of senna.** M. JOACHIMOWITZ. *Pharm. Presse* 28, 50-1, 57-8(1923).—A product emanating from a London firm was found to consist of senna  $\frac{2}{3}$ , and *Pluchea lanceolata*  $\frac{1}{3}$ , the latter resembling the true drug in many respects.

W. O. E.

**New derivatives of quinine.** A. HEFFTER. *Munch. med. Wochschr.* 68, 707-8 (1921); *Abstracts Bact.* 6, 153-4.—Certain quinine derivs. have been claimed to have sp. bacteriocidal action against staphylococci, streptococci, pneumococci and diphtherial bacilli. *Ethylhydrocupreine* (optochin) is a white powder insol. in water. Its hydrochloride is sol. 1:8. It is sp. for pneumococci. However, there is no proof yet that it acts etiotropically in human pneumonia, though it influences the fever and subjective state favorably. It has the disadvantage of occasionally producing a temporary amaurosis. Other obscure dangers are suspected. *Isoamylhydrocupreine* (cucupine) has the same soly. as optochin. It has a pronounced local analgesic action. No definite sp. effect has yet been shown for this compd. though it has been tried in diphtheria and influenza. *Isodetylhydrocupreine* (vucine) is strongly bacteriocidal against staphylococci and streptococci. It has been used successfully in 1:2000 soln. in gas infections. Stronger solns. are necrotizing. Its use is still in the exptl. stage.

H. G.

**Preliminary pharmacological assaying of unknown drugs.** JOHN GRÖNBERG. *Acta Med. Scand.* 56, 230-94(1922).—A discussion of simple methods for trying out drugs.

S. MORGULIS.

**Precipitate in infusum rhei opiatum.** POUL CLAUSSEN. *Arch. Pharm. Chem.* 30, 121-31(1923).—Infusum rhei opiatum F. n. c. H. 1913 (Ph. Dan.) is a mixt. of infus. rhei alk. 25 parts, Et<sub>2</sub>O 10 parts, and tinct. thebaic. crocat. 5 parts. A voluminous ppt. develops in this medicine. It could not be prepd. in such a way that no ppt. resulted. The ppt. besides contg. extractives, etc., contained narcotine, an essential component of the medicine. The prepn. must not be filtered and directions for shaking before use should be definite. The ppt. gave a positive test for hydroxymethylanthraquinone. At 8.1° this fluid mixt. can hold in soln. 1.56% Na<sub>2</sub>CO<sub>3</sub> and this amt. of carbonate is present from the prepn. of the first component of the medicine; it should, therefore, not be stored at a lower temp. than this.

A. R. ROSE.

**Brompton lozenges.** WM. A. KNIGHT. *Chemist & Druggist* 98, 411(1923).—The original lozenges, made from licorice ext., oil of anise and a lozenge mass of gum arabic,

tragacanth, sugar and rose water, were brown, kept firm in storage and, dissolving slowly, prolonged the local effect. Later, charcoal was added for uniformity of dark color. The modern compressed tablet tends to disintegrate and dissolve fast and irregularly; the color is often due to aniline black.

S. WALDBOTT

**Linimentum terebinthinae**, B. P. Wm. A. KNIGHT. *Chemist & Druggist* 98, 666(1923).—The official prepn. often forms a jelly on keeping, owing to lack of enough  $H_2O$  to hold the soap in soln. By setting aside for several days a mixt. of soft soap 0.5,  $H_2O$  2.5, camphor 1, oil of turpentine 14 oz., then shaking the 2 layers together frequently, a permanent emulsion is formed which may be dild. to 1 pint.

S. WALDBOTT

**History and evolution of pharmacy instruction in France.** L. GAUTIER. *J. pharm. Alsace-Lorraine* 49, 1-40(1922).—An address.

S. WALDBOTT

**Note on Boletus cervinus** (*Elaphomyces variegatus*, Vitt. and *E. granulatus*, Fries). E. REEB. *J. pharm. Alsace-Lorraine* 49, 137-42(1922).—This mushroom, reputed to be an aphrodisiac for cows, contained very small amts. of a glucoside and larger amts. of an alkaloid (*K*). Five kg. of boletus yielded 3360 g. of spores with mycelium and 1640 g. of fungus body ("coques") (*A*). The spores contained *mannitol*. To isolate *K* from *A*, sat. 95%  $EtOH$  with  $NH_3$  vapors, impregnate 60 g. powd. *A* with this soln.; after 24 hrs., dry completely in air. Treat with 100 g.  $AmOH$  on the water bath, cool, filter and shake out with dil.  $HCl$ . Remove fat with  $Et_2O$  and evap. the aq. soln. The yield of the  $HCl$ -salt of *boleterine* is 0.2%. The salt is amorphous, but forms crystals (sketched) after 1 week. The salts with  $H_2SO_4$  and  $HNO_3$  act similarly. The solus. ppt. with tannin, Mayer's reagent,  $I-KI$ ,  $K_2CdI_4$ , picric acid, etc., but not with  $HgCl_2$ . No aphrodisiac effect was observed in guinea pigs.

S. WALDBOTT

**Daucusin**, a bitter glucoside of the seeds of *Daucus carota*, L. E. REEB. *J. pharm. Alsace-Lorraine* 50, 13-5(1923).—Ground seeds of red carrots extd. with petr. ether (d. = 0.870) yielded 10% of a green, non-drying, bitter fatty oil, from which a fatty acid, "*daucusic acid*," sepd. on being in contact with filter paper for 2 weeks; white, feathery crystals formed, m.  $26^\circ$ , when purified with glacial  $AcOH$ . To isolate the bitter principle, macerate the ground red seeds with 80%  $EtOH$ , in which the fatty oil is insol. Press out, filter and evap. to dryness. Take up with  $H_2O$ , ppt. with  $Pb(AcO)_2$ , filter, almost neutralize with  $NH_4OH$ , filter again and sep. the  $Pb$  with  $H_2S$ . Filter, evap. to dryness, take up with  $H_2O$  and ppt. the glucoside with  $(NH_4)_2SO_4$  (*A*), wash it on a filter with a satd. soln. of *A*, then dry it and ext. with 90%  $EtOH$ , evap. this to dryness. Or, heat 10 g. of powd. red seeds at  $100^\circ$  for 1 hr. with 300 g. of milk of lime, filter, evap. to 30 g. and add 15 g. crystd. *A*, heat gently to dissolve it; after 12 hrs. filter the pptd. glucoside and wash with soln. of 50 g. *A* in 100 g.  $H_2O$ . Then dry and ext. with 95%  $EtOH$ , evap. the soln. *Daucusin* is a yellow, non-hygroscopic powder, very bitter, sol. in  $EtOH$ , less sol. in  $H_2O$ , is colored violet with concd.  $H_2SO_4$ , lavender with  $HCl$ , yellow with  $HCl$  and  $FeCl_3$ , etc. Hydrolysis with dil.  $H_2SO_4$  yields an amorphous substance, turning red with  $H_2SO_4.H_2O$ , and probably differing from cryst. carotin.

S. WALDBOTT

**Hydrargyri oxycyanidum**, Brit. Pharm. Codex. F. C. J. BIRD. *Pharm. J.* 110, 383-4(1923).—The process of the B.P.C. leads to the "normal" compd.  $HgO.Hg(CN)_2$  (I); the tests of the Swiss pharm. point to the "cryst." compd.  $HgO.3Hg(CN)_2$  (II). I being explosive, its prepn. is dangerous, while that of II, with due care, is not. II keeps better than I; it does not readily blacken when stored, is more sol., and is equally effective as an antiseptic. In sterilizing surgical instruments, a weak soln. of II will attack steel slightly after 24 hrs.; a fairly strong soln. causes corrosion after 15 min.; but the addition of  $Na_2CO_3.10H_2O$  (1% of the wt. of II) prevents corrosion even on several days' contact. II will be adopted in the new B.P.C. (cf. Jones, C. A. 14, 2896).

S. WALDBOTT

**Stabilization of drugs.** H. GOLAZ. *Schweiz. Apoth. Ztg.* 61, 127-30, 135-8. C. FLEISCHMANN. *Ibid.* 61, 174-5(1923); cf. C. A. 3, 226; 16, 2008.—The methods, advantages and applications of the stabilization of drugs are described. Standard fluid-exts. prepd. from stabilized drugs, e. g., belladonna or hyoscyamus, could be used for the prepn. of standard tinctures, sirups, ointments and solid exts. of prescribed strengths. F. recommends exposing the drugs to  $SO_2$  vapors in a closed space.

S. WALDBOTT

**Suggestions anent the pending Swiss pharmacopeia.** L. ROSENTHALER. *Schweiz. Apoth. Ztg.* 61, 133-5(1923).—Thermometers used for detg. m. p. and b. p. should be examd. by practical standard methods, e. g., comparison with the m. p. of ice and a standard scale of m. p. of pure substances. Addition of preservatives, e. g., to  $H_2O_2$  or galenical prepn. should be allowed instead of requiring these freshly prepd. Domestic drugs that are apt to replace foreign drugs should become official. In prep. *spiritus*

*cachlearias* from dry herb, add some white mustard seed to replace the enzyme and make the herb always available. In detg. ash, detn. of HCl-insol. matter should be added in many cases. Extracta spissa, excepting ext. filicis, should be dropped.

S. WALDBOTT

**New relationship between Papaveraceae and Berberidaceae revealed by chemical and pharmacodynamic studies.** H. GUYOT. *Schweiz. Apoth. Ztg.* 61, 146-50 (1923).—The structural formulas of narcotine and hydrastine show close chem. relationship, and both alkaloids depress the tonicity of smooth muscle. The corresponding oxidation products, cotarnine and hydrastinine, closely related to each other, possess styptic properties.

S. WALDBOTT

**Formaldehyde soap solutions.** THOMANN. *Schweiz. Apoth. Ztg.* 61, 181-2 (1923).—Com. lysoform contains 4.0% HCHO (7.2-8% in 1905). The disinfecting power of even a 10% lysoform solu. is inferior to that of a 1% PhOH or 0.1% HgCl<sub>2</sub> solu. S. W.

**Stabilization and the extract question.** J. LANG. *Schweiz. Apoth. Ztg.* 61, 205-7 (1923).—Cultivation, collection and working-up of the drugs to be stabilized demand scientific control. Pharm. Helv. V should require stabilization at least for some drugs. Fluidexts. should be adopted, and extracta spissa dismissed, owing to chem. changes in their prepn.

S. WALDBOTT

Origin of essential oils in living plants (SIMPSON) 11D. Chemistry of certain Australian plant products (SMITH) 11D.

REUTTER, L.: *Traité de matière médicale et de chimie végétale*. Parts IV, V and VI, each P. 12. Paris, Vie: J. Baillière et Fils. Reviewed in *Pharm. J.* 110, 342 (1923).

**Double compounds of 1-allyl-3,7-dimethylxanthine.** E. PREISWERK. U. S. 1,455,204, May 15. At least 2 mol. proportions of Na salicylate or Na or Li benzoate or other alkali salt of a benzenecarboxylic acid is permitted to react upon 1-allyl-3,7-dimethylxanthine. The products are sol. in H<sub>2</sub>O; their dil. aq. solns. are neutral and are not decomposed by alkalies while the addition of acid produces a cryst. white ppt. On intense heating the products leave a residue which is solid and of alk. reaction. These double compds. are diuretic and analeptic therapeutics.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

**The alkali industry centenary.** ANON. *Chemist & Druggist* 98, 581-2 (1923).—Historical notes on the development of the alkali industry with portrait of the founder James Muspratt, 1793-1886.

S. WALDBOTT

**The catalytic oxidation of ammonia by air in contact with platinum.** EUGÈNE DECARRIÈRE. *Ann. chim.* 18, 312-88 (1922); cf. *C. A.* 14, 2395; 16, 2011.—A descriptive bibliography of 26 references is given. A study was made of the influence on the yield of oxides of N of the following factors: form of the Pt catalyst, temp. of reaction, time of contact, compn. of NH<sub>3</sub>-air mixt., and the presence of certain gaseous impurities in com. NH<sub>3</sub> from CaCN<sub>2</sub>. For each catalyst there was found an optimum temp. interval and either an optimum interval or an upper optimum limit for the NH<sub>3</sub> content of the gas mixt. Acetylene, H<sub>2</sub>S, and PH<sub>3</sub> decrease the yield of oxides of N and hasten the wearing out of the catalyst.

F. L. BROWNE

**The history of the ammonia process.** MAX TRAUTZ. *Naturwissenschaften* 11, 339 (1923).—Polemical. Haber's criticism (cf. *C. A.* 17, 1110) of Trautz's text-book is not justified. FRITZ HABER. *Ibid* 339-40.—A reply. The text of the original patent is given.

C. C. DAVIS

**The nitrogen problem.** ANON. *J. four. elec.* 32, 43-5, 51-2 (1923).—A review.

C. G. F.

**The scientific development of the potash salt industry.** O. F. F. NICOLA. *Anales assoc. quim. Argentina* 10, 403-24 (1922).—A general review of sources and methods of production of crude potash salts throughout the world, including possible future or emergency sources.

L. E. GILSON

**Trend of the price of potash in Germany in the years 1861 to 1923.** A. JACOB. *Chem.-Ztg.* 47, 377-9 (1923).

E. J. C.

**Beryllium salts.** ALBERT HUTIN. *Rev. prod. chim.* 26, 257 (1923).—Brief outline of their extrn. and utilization.

A. PAPINEAU-COUTURE

**The manufacture of sodium thiosulfate.** L. HARGREAVES AND A. C. DUNNINGHAM. *J. Soc. Chem. Ind.* **42**, 147-52T (1923).—The manuf. of  $\text{Na}_2\text{S}_2\text{O}_3$  from  $\text{Na}_2\text{SO}_3$  and S is described. A process is given for the manuf. of  $\text{Na}_2\text{S}_2\text{O}_3$  from  $\text{SO}_2$ ,  $\text{Na}_2\text{CO}_3$  and S in one stage. A schematic design of a plant for each process and notes on their operation are also presented.

R. L. BROWN

**Norwegian dolomite. Utilization of dolomite.** OLAF HOLTHEDAH, AND OLAF ANDERSEN. *Norg. Geol. Undersökelse, Statens Raastofkomite Publication No. 2*, 49 pp. (1922).—Deposits of fine-grained dolomite occurring in the northern part of Norway are described. Some preliminary expts. on the "burning" of dolomite have been carried out. The heating of this dolomite for 2-5 hrs. at  $1400^\circ$  produced no effective sintering. The structure of the raw dolomite has no great influence on the structure of the burned product, since, within certain limits, the resulting lime and magnesia were always very fine-grained. The sepn. of lime from raw dolomite by elec. sintering or melting is discussed.

J. A. ALMQUIST

**Sulfide ores in Sweden.** AXEL GAVELLIN. *Teknisk Tids. Bergsvetenskap* **53**, 13-20(1923).—A preliminary report of a survey of recently discovered pyrites in one of the Swedish provinces. The ore carries Cu and Zn. A map gives the locations of pyrites mines (producing and non-producing), and sulfite and  $\text{H}_2\text{SO}_4$  factories of the Scandinavian countries and Finland.

A. R. ROSE

**The significance of industrial hydrogen.** *Chem. Met. Eng.* **28**, 931(1923).—An editorial interview with H. S. Taylor.

E. J. C.

**Anti-dimming preparations for glass surfaces.** H. A. KUHN. *Chem. Met. Eng.* **28**, 762-3(1923).—Two anti-dimming preps. have been developed as substitutes for the sulfonated castor oil product used during the war. They consist of the Na salts of rapeseed or cottonseed oils, NaOH, glycerol, sodium silicate and engine oil. The prep. is applied in stick form or impregnated in a loosely knit cotton cloth. The anti-dim testing machine is described and illus.

W. H. BOYNTON

CUMMING, ALEXANDER CHARLES: **Manufacture of Hydrochloric Acid and Salt-cake.** Vol. V. London: Messrs. Gurney & Jackson. 423 pp. 31s. 6d. net.

WYLD, WILFRED: **Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide.** Vol. I. London: Gurney & Jackson. 558 pp. 36s. net.

**Acid receiver.** P. L. PFANNENSCHMIDT. U. S. 1,454,945, May 15. Receivers for acid, e. g.,  $\text{H}_2\text{SO}_4$ , HCl or  $\text{HNO}_3$ , are formed of a rigid framework of acid-resisting material such as passive Fe the openings of which are covered with relatively thin plates of acid-proof material, e. g., sheet metal.

**Ammonia synthesis.** A. NAGELVOORT. U. S. 1,454,591, May 8. H and N which are to be used for the synthesis of  $\text{NH}_3$  are preliminarily purified and dried by contact with products formed by heating dry  $\text{Ca}_2\text{Fe}(\text{CN})_6$  or a similar cyanide to  $450$ - $500^\circ$ .

**Ammonia synthesis.** J. C. CLANCY. U. S. 1,454,599, May 8. An active catalyst for use in  $\text{NH}_3$  synthesis is prep. by activating a cyanide material, e. g., by treating pumice stone with a soln. formed from  $\text{H}_2\text{O}$ , Ca ferrocyanide and Ba ferrocyanide, drying and gradually heating in H and N to about  $350^\circ$ . Cf. C. A. 17, 857.

**Rendering stable alkaline solutions containing active oxygen.** A. SCHAIDHAUF. Can. 230,967, May 8, 1923. Alk. solns. contg. active O are stabilized by the addition of a colloidal Mg compd. or a colloidal combination of MgO and  $\text{SiO}_2$ .

**Ammonium perchlorate.** R. A. LONG. U. S. 1,453,984, May 1. A "nucleus soln." contg.  $\text{NH}_4\text{ClO}_4$  9-12,  $\text{NaClO}_4$  1-7 and NaCl 17-22% is treated with sufficient  $\text{NaClO}_4$  and  $\text{NH}_4\text{Cl}$  to produce a soln. contg.  $\text{NH}_4\text{ClO}_4$  18-30,  $\text{NaClO}_4$  1-7 and NaCl 17-22% and the NaCl which seps. is removed. The remaining liquid is dild. and  $\text{NH}_4\text{ClO}_4$  is sepd. from it at a temp. below  $30^\circ$ .

**Magnesium nitrate.** V. M. GOLDSCHMIDT. U. S. 1,454,583, May 8. See Can. 216,799 (C. A. 16, 1839).

**Anhydrous metal chlorides.** B. S. KIRKPATRICK AND F. S. MORGAN. U. S. 1,455,005, May 15. The metal to be chloridized, e. g., Al, is alloyed with Zn or other metal having a chloride-forming or vaporizing temp. higher than that of the first metal and the alloy (which has a m. p. between the chloride-forming and vaporizing temp. of the first metal) is treated with Cl while the alloy is molten.

**Arsenical compounds.** K. B. EDWARDS. Can. 230,158, Apr. 10, 1923. As compds. of the general formula  $\text{RASOS}_2$ , where R is an alkali metal or  $\text{NH}_4$  are prep.

by treating  $As_2O_3$  with an alkali polysulfide and reducing the salts to an anhyd. form by evapn. under reduced pressure. Cf. C. A. 16, 2583.

**Refining selenium oxychloride.** G. J. FINK and E. D. CHAUGUR. U. S. 1,453,789, May 1.  $SeOCl_2$  is purified by distn. in an atm. contg. an excess of Cl.

**Zirconium dioxide.** O. RUFF. U. S. 1,454,564, May 8. A Zr ore is heated to 1200–1400° with  $Na_2CO_3$  in the proportion of 0.75–2 mol. equivs. of the  $Na_2CO_3$  for each mol. equiv. of Zr oxide in the ore and about 1–1.5 mol. equivs. of the  $Na_2CO_3$  for each mol. equiv. of  $Al_2O_3$  and  $SiO_2$ .  $H_2O$ -insol. Zr compds. are dissolved in hot  $H_2SO_4$  and Zr hydroxide is pptd. and used to make  $ZrO_2$ .

**Iron oxide from spent iron sludge.** C. V. BACON. U. S. 1,455,060, May 15. Fe sludge such as is obtained in aniline production or similar processes is heated in pasty condition with  $H_2SO_4$  to conc. the acid and produce a porous spongy mass which is then roasted to recover oxide of Fe and S oxides. Cf. C. A. 16, 3737.

**Carbon disulfide.** A. E. DELPH. U. S. 1,454,708, May 8. A retort formed of ferrous metal with a firmly adherent coating of Al on its inner surface is used for production of  $CS_2$  from S and C at about a red heat. The Al coating serves to prevent attack of the retort wall by the S.

**Handling chlorine.** H. C. P. WEBER. U. S. 1,454,873, May 15. A satd. soln. of Cl or  $CCl_4$  contg. a dissolved catalytic agent such as I, S or a metal chloride is used for convenient shipment and storage and use in "step-wise" chlorination of  $CH_4$ ,  $C_2H_4$  or other materials.

**Solidifying molten sulfur.** R. H. STEWART. U. S. 1,454,344, May 8. S obtained by underground fusion is cast into relatively small thin cakes when the molten material is brought to the surface of the ground and the cakes are allowed to cool and at least partially solidify upon a conveyor.

**Burning sulfur.** H. S. DAVIS. U. S. 1,455,284, May 15. A combustion-accelerating material such as asbestos or porous "nonpareil" brick is mixed with crude oil-contaminated S to promote its combustion in open pans or other burners. Cf. C. A. 17, 2035.

**Apparatus for making flowers of sulfur.** E. KNAPP, J. K. DICKERSON and F. L. BEGRUP. U. S. 1,454,747, May 8. A trap for collecting liquid S is placed within a chamber to which S vapors are supplied, adjacent to the vapor inlet.

**Production of reducing gases.** J. E. LEONAKZ. Can. 230,651, May 1, 1923. Oxide of Fe and C is heated without excess of air and the resultant gas is passed through a molten bath to which C is added.

**Carbonaceous catalyst from hydrocarbons and chlorine.** E. H. PAYNE and S. A. MONTGOMERY. U. S. 1,453,766, May 1. Cl is passed through a paraffin distillate or similar hydrocarbon material at a temp. of about 150° until a coal-like solid mass is formed which is suitable for catalyzing chlorination of gas.

**Transparent agar-agar product.** C. MATSUOKA. U. S. 1,453,848, May 1. Suitable sea-weed material is dried and treated with Cl until bleached, then treated with  $Na_2S_2O_3$ , washed in  $H_2O$  and then treated with heated  $H_2O$  to produce a homogeneous and viscous mass. The latter is subdivided by passing it through a sieve, dried and dipped in cold  $H_2O$  to effect a further bleaching and then again dried, to obtain a transparent product. Cf. C. A. 16, 766.

**Acid mixture for treating files.** A. N. J. ZIRSEN. U. S. 1,454,369, May 8. See Can. 225,244 (C. A. 17, 188).

**Detergent composition.** M. V. NEEDLE. U. S. 1,455,350, May 15. A compn. adapted for cleaning stained gloves is formed of  $ZnO$  5, aqua  $NH_3$  5,  $MgCO_3$  3, neat's-foot oil 2 and alc. 1 part.

**Carbon-removing composition.** H. W. EASTMAN. U. S. 1,455,574, May 15. A mixt. for use in removing C deposits from engines or spark plugs is formed of alc. 80, acetone 15, ether 4, strong ammonia water 100 and  $CHCl_3$  4 parts.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**Glass-forming machines.** C. SAXTON. *Pottery Gaz.* 43, 629–34(1923).—A very complete description of the principles of various glass-mfg. machines and the methods employed in the production of the various types of glass ware. J. W. HEPPLEWHITE

**Catalysis in glass formation.** E. GERLACH. *Chem.-Zig.* 47, 146(1923).—F and

Sb are said to have a catalytic action in the formation of glass as is shown by the fact that the coeffs. of expansion of glasses are smaller than values calcd. from the factors given by Hovestadt (*Jenaer Glas.* 1900). The use of F reduced the coeff. of expansion of a borosilicate glass from  $80 \times 10^{-7}$  to  $77 \times 10^{-7}$  by actual expt. and with Sb the result was a reduction from  $74 \times 10^{-7}$  to  $33 \times 10^{-7}$ . No expl. details are given. The fact that most of the Sb in a glass can be extd. by various solvents is considered proof that it is not part of the glass mols. It is suggested that either a rearrangement of the polysilicate mols. may take place, or that the action may be a packing effect only, as in the case of a small amt. of Th in W.

G. E. BARTON

**Heat-resisting glasses.** W. E. S. TURNER. *J. Roy. Soc. Arts* 71, 401-12; *Glassworker* 42, No. 30, 13, 21, 22, 24, 26(1923).—A discussion of the whole subject. The whole work done at Jena, establishing the relationships between the mechanical properties and chem. compn. in glasses, needs revision. Also in *Potter Gas.* 48, 607-17 (1923).

G. E. BARTON

**Manufacture of colorless glass in a tank furnace.** F. W. ADAMS. *J. Soc. Glass Tech.* 6, 205-10(1922); *Pottery Gaz.* 47, 1031, 1033.—The tank should be long enough and deep enough to melt and "fine" the charge properly before it is passed through the "doghole." The working end should hold slightly more than the estd. daily output. Good refractories are essential, as modern machines need a fairly soft and therefore corrosive batch. A batch with a high content of soda ash corroded blocks of high silica content more than blocks of high alumina content in the same furnace. A block which withstood the action very well was close grained and had the compn.  $\text{SiO}_2$  58.9,  $\text{Al}_2\text{O}_3$  37.58,  $\text{Fe}_2\text{O}_3$  1.71,  $\text{CaO}$  0.54,  $\text{MgO}$  0.47,  $\text{Na}_2\text{O}$  0.36,  $\text{K}_2\text{O}$  0.84%. The necessity for regular chem. supervision of batch materials and for thorough mixing and accurate weighing is emphasized.  $\text{MnO}_2$  is a cheaper decolorizer than Se, but is affected by furnace conditions, e. g., by standing over the week-end. With Se quick melting is essential to prevent loss by volatilization. The coloring effect is regarded as due to colloidal particles of Se sepg. out. The melting temp. is detd. by the type of batch used and by the output, but is normally about 1350-1400°. More Se is needed at lower temps., with the danger of producing a dirty brown color, which with a rise in temp. of the tank turns to a decided pink. The Se glass in thelehr if too cold becomes green, and if too hot pink. Storage of Se glass in strong sunlight has been known to produce a yellow color, which can only be removed by re-melting. A. recommends the stabilization of working conditions as far as possible once they have been worked out for a given amt. of iron in the batch. For discussion see *Pottery Gaz.* 47, 1208-10.

J. S. C. I.

**Density of soda-lime-magnesia glasses and calculation of density.** S. ENGLISH AND W. E. S. TURNER. *J. Soc. Glass Tech.* 6, 228-31(1922).—The substitution of magnesia for lime in the trisilicate glasses brought about a continuous lowering of the d. without any sign of a minimum value, such as was observed in the case of the annealing temps. Baillie's proposal (*C. A.* 15, 3374) of the formula  $A/D = p_1/d_1 + p_2/d_2 + p_3/d_3 + \dots$  instead of Schott's,  $100/D = p_1/d_1 + p_2/d_2 + p_3/d_3 + \dots$ , A being the sum of the oxides, gave good results, but the authors' method (*C. A.* 14, 3509) had a more definite basis in that the d. of silica was assumed unchanged in the glass and from that the soda, lime, magnesia, etc., factors could be calcd. by using a plain soda silicate and then a soda-lime silicate, etc. Results obtained by Schott's, Baillie's, and the authors' methods were compared with observed values and it was shown that while Schott's method gave greatly divergent values, those obtained by Baillie's method were very near, and those by the authors' method still nearer, the observed values.

J. S. C. I.

**Mixing of glass batches in factories.** A. W. DICKENSON, V. DIMBLEBY, L. E. NORTON, AND W. E. S. TURNER. *J. Soc. Glass Tech.* 6, 234-46(1922).—The grain size of all constituents should preferably be similar. Very fine sand and in some instances very fine lime should not be included, as they contain undesirable impurities. The danger of segregation of perfectly dry batch when stored in hoppers over the "doghouse" of a tank furnace is pointed out and also the beneficial effect of moisture, up to a point, in preventing this. Various analyses of batches mixed by hand and by 3 different types of mixing machines showed a decided superiority as regards homogeneity of the machine-mixed batch over that mixed by hand.

J. S. C. I.

**Composition of limes suitable for glass-making.** V. DIMBLEBY AND W. E. S. TURNER. *J. Soc. Glass Tech.* 6, 221-8(1922).—Working on the assumptions that the limit of  $\text{Fe}_2\text{O}_3$  which can be decolorized in a pot is the same as that which can be decolorized by Se in a tank furnace, i. e., 0.09%, that  $\text{Fe}_2\text{O}_3$  taken up during melting in the furnace is 0.03%, and that the soda ash introduces 0.015%, the authors calcd. the per-

missible amts. of  $\text{Fe}_2\text{O}_3$  in limestone for sands of various iron contents. From calcns. of representative batches, the max. permissible for a decolorized glass was found to be 0.18%, but this is regarded as a dangerously high figure in practice. Samples quoted ranged from a Dowlow (Buxton) limestone with  $\text{Fe}_2\text{O}_3$  0.01% (non-volatile insol. matter 0.32%) to a soapworks waste with  $\text{Fe}_2\text{O}_3$  0.10% (non-volatile matter 0.51%). For pale green glass suitable samples ranged from Barnetby limestone with  $\text{Fe}_2\text{O}_3$  0.14% (non-volatile matter 1.94%) to a chem. works waste with  $\text{Fe}_2\text{O}_3$  0.32% (non-volatile matter 3.62%) while for a dark green bottle glass the limes with high  $\text{Fe}_2\text{O}_3$  content were desirable as, in conjunction with a low-grade sand, they supplied the bulk of the coloring oxide needed in the glass.

J. S. C. I.

**British glass industry; its development and outlook.** W. E. S. TURNER. *J. Soc. Glass Tech.* 6, 108-46 (1922).—Presidential address, contg. an account of the history of the industry with statistics as to number of factories, workmen, production, exports, imports, etc.

**Problems in the melting of glass. II. Discussion.** *J. Soc. Glass Tech.* 6, 147-56 (1922).—(1) *Best ratio of cullet to batch.* When batch alone is used, the glass takes longer to plain and is also somewhat softer. It may contain very fine seed which affects its working properties. The cullet contains more iron and more alumina than the batch, therefore it makes the glass more colored and more viscous, but it helps in plaining. Practice varies widely, depending largely on the amount of cullet available. In the case of tank furnaces, the important thing is to keep the ratio constant so that the properties of the glass will not change. (2) *Salt cake vs. soda ash in soda-lime glass batches.* Although no scientific explanation is at present available, it is a matter of experience that glass made from batch containing salt cake is easier to work, and apparently has a longer viscosity range than if soda ash alone is used. It was suggested that this is due to greater homogeneity. It is American practice in making window glass to use 1 part salt cake to 2 parts soda ash. However, the salt cake is more corrosive of the refractories and sometimes gives a bluish green color.

**Columnar structure in sandstone tank blocks after rapid heating and cooling.** JOHN CURRIE. *J. Soc. Glass Tech.* 6, 150-60 (1922).—Blocks forming the lower course of the walls of a green bottle glass tank became rapidly heated from about 800° to 1300° during the draining of the tank and were then rapidly cooled. They were found to show a columnar structure normal to the cooling planes, similar to that of basaltic columns. Four photographs are reproduced.

**Medieval glass of York Minster.** W. F. NORRIS. *J. Soc. Glass Tech.* 6, 160-7 (1922).—York Minster has over 25,000 sq. ft. of English glass of the 13th, 14th and 15th centuries. During the War, 23 windows were removed for preservation, and it was then found that the lead had disintegrated and the glass seemed to be diseased, many pieces being badly pitted and some having scaled off until they were paper thin; others had crumpled to dust. The windows were being gradually cleaned and releaded, the mellowing effect of centuries of dirt being removed but the original brilliancy being restored. W. E. S. Turner explained the disease as due to a gradual hydration of the glass, which was doubtless a lime glass made from French sand with perhaps not much alumina.

**Experiments on the manufacture of pure white hard porcelain.** MIKIYA AKAT-SUKA. *Report of the Pottery Lab., Kyoto*, No. 1, 1-13 (1922).—Many expts. were made to produce pure white porcelain with Korean kaolin as its chief raw material. The firing temp. was Cone 14 throughout the study. **Raw materials.** Korean kaolin of Daiyamen, Katogun, Keishonando, Gairome clay (highly plastic kaolin) of Tokiguchi, feldspar and quartz of Ehime prefecture, and talc of South Manchuria were used. The Korean kaolin analyzed: 45.06  $\text{SiO}_2$ , 38.44  $\text{Al}_2\text{O}_3$ , 0.54  $\text{Fe}_2\text{O}_3$ , 0.73  $\text{CaO}$ , 0.16  $\text{MgO}$ , 0.80 alkalies and 14.32% loss on ignition. **Compn. of body.** Its range was clay 54-67% (kaolin 33-53%, Gairome clay 6-21%), feldspar 21-29% and quartz 12-18%. These materials were used in air-dry state. The content of moisture was as follows: kaolin 6.64%, Gairome clay 6.32%, feldspar 0.20%, quartz 0.08% and talc 0.08%. **Glaze formula.** Glazes tried were 0.65  $\text{K}_2\text{O}$ , 0.35  $\text{MgO}$ , 0.75-0.90  $\text{Al}_2\text{O}_3$ , 9.5-10.0  $\text{SiO}_2$ ; 0.70  $\text{K}_2\text{O}$ , 0.30  $\text{MgO}$ , 0.8-1.2  $\text{Al}_2\text{O}_3$ , 9.0-12.0  $\text{SiO}_2$ ; 0.75  $\text{K}_2\text{O}$ , 0.25  $\text{MgO}$ , 1.0  $\text{Al}_2\text{O}_3$ , 9.0  $\text{SiO}_2$ ; and 0.80  $\text{K}_2\text{O}$ , 0.20  $\text{MgO}$ , 0.85-0.95  $\text{Al}_2\text{O}_3$ , 8.5  $\text{SiO}_2$ . They were composed of feldspar, Gairome clay, talc and quartz. **Glazing.** Glaze slips rich in feldspar are liable to settling. Therefore, a small amt. of  $\text{AcOH}$  (about 20-30 cc. for 72 liter cask) was added. Its effect is not temporary as that of  $(\text{NH}_4)_2\text{CO}_3$ . Suitable grinding time for bodies was 25 hrs. and for the glaze 35 hrs. with a 100 kg. wet grinding cylinder. Talc has to be ground for 20 hrs. before it is used in glaze batches. The 3 following bodies were excellent with respect to forming, cracking in drying and burning color:



Korean kaolin 33, 38, 44, Tokiguchi Gairome 21, 17, 19, Ehime feldspar 28, 28, 23, Ehime quartz 18, 17, 14%, resp. Glazes of the formulas  $0.65 \text{ K}_2\text{O}$ ,  $0.35 \text{ MgO}$ ,  $0.90 \text{ Al}_2\text{O}_3$ ,  $10.0 \text{ SiO}_2$ ;  $0.70 \text{ K}_2\text{O}$ ,  $0.90 \text{ Al}_2\text{O}_3$ ,  $10.0 \text{ SiO}_2$ ;  $0.70 \text{ K}_2\text{O}$ ,  $0.30 \text{ MgO}$ ,  $1.20 \text{ Al}_2\text{O}_3$ ,  $11.0 \text{ SiO}_2$ ; and  $0.70 \text{ K}_2\text{O}$ ,  $0.30 \text{ MgO}$ ,  $1.20 \text{ Al}_2\text{O}_3$ ,  $12.0 \text{ SiO}_2$  were satisfactory. The last glaze which was best was further improved in color and luster by partly replacing the Gairome clay with the kaolin. The batch was as follows: Ehime feldspar 41.4, Tokiguchi Gairome 8.0, Korean kaolin 5.7, Manchurian talc 4.0 and Ehime quartz 40.8. Most of 27.4 cm. plates shrank to 24.6 cm., of which 0.1 cm. was due to glaze layers, in drying and burning.

S. KONDO

**Study of translucent hard fayence glaze.** JISUI UVEDA. *Rept. of Pottery Lab., Kyoto No. 1*, 14-56(1922).—The purpose was to produce a hard fayence with an appearance of porcelain by improving the glaze and also by coloring both body and glaze. Cryolite tends to produce devitrified spots. Otherwise, the result was good. Fluorspar acted like cryolite. The use of an engobe composed of 49.5% fluorspar, 41.3% feldspar and 9.2% Gairome clay under a transparent glaze is promising, though uniform application of the engobe was not accomplished.  $\text{SnO}_2$  makes the glaze mat or gives an appearance like an enamel.  $\text{Sb}_2\text{O}_3$  behaves like  $\text{SnO}_2$ . Zirconia acts like  $\text{SnO}_2$ , but produces a bluish shade instead of yellow.  $\text{ZnO}$  acts only weakly as an opacifier, but makes the glaze white and bright. *Compound opacifiers.* Satisfactory results were first obtained with glazes contg. 3%  $\text{SnO}_2$  and 5% fluorspar or cryolite. Starting with the results, effects of variation in the amts. of  $\text{SnO}_2$ ,  $\text{F}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  were studied. The following proved best at Cone 01a: 0.32  $\text{PbO}$ , 0.10  $\text{K}_2\text{O}$ , 0.20  $\text{Na}_2\text{O}$ , 0.38  $\text{CaO}$ , 0.30  $\text{Al}_2\text{O}_3$ , 3.60  $\text{SiO}_2$ , 0.40  $\text{B}_2\text{O}_3$ , 0.15  $\text{F}$ , 0.063  $\text{SnO}_2$ . The batch was composed of 49.40% frit, 10.17%  $\text{PbO}$ , 11.17% Korean kaolin, 1.74% Gairome clay and 27.52% quartz. The formula of the frit was 0.191  $\text{PbO}$ , 0.119  $\text{K}_2\text{O}$ , 0.238  $\text{Na}_2\text{O}$ , 0.452  $\text{CaO}$ , 0.119  $\text{Al}_2\text{O}_3$ , 1.380  $\text{SiO}_2$ , 0.476  $\text{B}_2\text{O}_3$ , 0.178  $\text{F}$ , 0.075  $\text{SnO}_2$ . 0.0475  $\text{Fe}_2\text{O}_3$  and 0.00380  $\text{Co}_2\text{O}_3$  were added to 100 frit batch.  $\text{SnO}_2$  and  $\text{ZnO}$  gave excellent results with a glaze 0.32  $\text{PbO}$ , 0.10  $\text{K}_2\text{O}$ , 0.20  $\text{Na}_2\text{O}$ , 0.38  $\text{CaO}$ , 0.30  $\text{Al}_2\text{O}_3$ , 3.60  $\text{SiO}_2$ , 0.40  $\text{B}_2\text{O}_3$ , 0.12  $\text{ZnO}$ , 0.063  $\text{SnO}_2$ , composed of 50.0% frit, 10.1%  $\text{PbO}$ , 11.0% Korean kaolin, 1.7% Gairome clay of Tokiguchi and 27.2% quartz, for Cone 01a-02a. The formula of frit was 0.190  $\text{PbO}$ , 0.119  $\text{K}_2\text{O}$ , 0.238  $\text{Na}_2\text{O}$ , 0.453  $\text{CaO}$ , 0.119  $\text{Al}_2\text{O}_3$ , 1.370  $\text{SiO}_2$ , 0.476  $\text{B}_2\text{O}_3$ , 0.143  $\text{ZnO}$ , 0.075  $\text{SnO}_2$ , 0.0450  $\text{Fe}_2\text{O}_3$  and 0.0045  $\text{Co}_2\text{O}_3$  were added to 100 frit batch. By substituting 0.07  $\text{ZnO}$  for 0.063  $\text{SnO}_2$  in the first formula given above, a good glaze was obtained. However, it was deficient in luster. This was improved by increasing the fluorspar. Expts. with bone-ash and cryolite or fluorspar gave pretty good results, though the glazes were far inferior in translucency, luster and color to those with  $\text{SnO}_2$  and fluorspar. The use of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  or  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  for coloring the body is described. A good body was: 60.0% liparite of Amakusa, 18.0% Gairome clay of Tokiguchi, 17.0% amalgamite of Mitsuishi, 5.0% feldspar and 0.058% cryst. Co nitrate (0.015%  $\text{Co}_2\text{O}_3$ ). The batch was ground wet for several hrs. in a grinding cylinder. Then 0.0712% cryst.  $\text{Na}_2\text{CO}_3$  was added and ground again. The usual way of adding Co oxide to frit in glaze coloring is not satisfactory, as it produces a blue with purplish grey shade. Therefore various mixts. were tried. Ba chromate gave the greenish blue of porcelain glazes. For glazes contg.  $\text{SnO}_2$  the use of a mixt. of  $\text{Co}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in amts. of 0.0025-0.003% and 0.025-0.03%, resp., in matured glazes is recommended. S. KONDO

**Uranium glazes.** MIKIYA AKATSUKA. *Rept. of Pottery Lab., Kyoto No. 1*, 57-73 (1922).—Vermilion glaze. Raw glaze composed of 35  $\text{Pb}_2\text{O}_3$ , 10 quartz and 8  $(\text{NH}_4)_2\text{U}_2\text{O}_7$  produced a brilliant vermillion at Cone 012a-011a. An addn. of Funori glue is recommended. It was applied three times as thick as ordinary porcelain glazes on vitrified porcelain biscuits. Red glaze. By replacing 1 part of the uranate with 1 part of  $\text{Fe}_2\text{O}_3$  in the glaze, a brownish red was obtained. The appearance of the glaze changed with firing temp., thus:

Cone.	012a.	01a.	1a.	1a-2a.	5a.	8-9.
Fuel	wood	coal	wood	coal	coal	coal
Color of glaze	vermillion	reddish orange	blackish brown	reddish brown, blackish brown or reddish orange crimson or green	yellowish green, vermillion or blackish red green	blackish brown
Color of crystal	..	..	gold	..	..	..
Color of luster	..	..	..	..	greenish purple	gold or purple

Crystal glazes. The following table shows glaze batches and temps. at which crystal glazes were developed:

Glazes.	P.	Q.	Q.	R.	S.
Pb <sub>2</sub> O <sub>3</sub>	70	75	75	70	70
(NH <sub>4</sub> ) <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	16	15	15	15	16
Quartz	20	19	16	18	20
Rutile	7	7	8	3	..
Co carbonate	..	0.5	1	..	0.5
ZnO	..	..	..	5	..
Cone	5a, 6a	5a	5a, 6a	5a, 8	1a

When a vase was glazed with R, set in a sagger which was coated with a glaze composed of 37 Pb<sub>2</sub>O<sub>3</sub>, 8 quartz and 11 (NH<sub>4</sub>)<sub>2</sub>U<sub>2</sub>O<sub>7</sub> and burned to Cone 5a, very fine small golden crystals were developed on a bright glaze of the same color. S. KONDO

**Comparative examination of the structure of Japanese and foreign porcelains.** R. SHIGEMUNE. *Tokio Industrial Lab., Rept. XVII, No. 6, 59 pp.* (1922).—Microstructure of 33 Japanese and 24 foreign porcelains, mostly table wares, has been examd. Japanese porcelains may be classified into 2 groups: (a) Porcelain made of plastic clay, feldspar and weathered granite. Thin sections are usually light brown and have sillimanite in their ground-mass. (b) Porcelain mainly made of decompd. acid rock. Porcelain which has been mainly made of weathered liparite has no sillimanite in the ground-mass, though its feldspar grains are rarely sillimanitized. It is generally fine-grained and is light grey or white. The microstructure of Kutani wares, which are made of Hanasaka rock (weathered quartz-prophyry) 5-6, Gokokuji rock (weathered quartz-prophyry) 4-5 and Nabetani clay 3-6, resembles that of porcelain (a). Pores in the European porcelains are generally less in number and smaller than those in Japanese wares. Generally speaking, quartz grains in the European wares are smaller than those in Japanese porcelains and have a glassified outline, while only a few Japanese porcelains show similar structure. The European porcelains are generally superior to the Japanese in this respect. Japanese porcelains are generally superior to European in translucency. S. KONDO

**Glass and metal.** W. E. S. TURNER. *Metal Ind.* (London) 22, 128 (1923).—Glass mfg. processes were contrasted with those in steel manuf. in a lecture. Corrosion of glass and of metals are contrasted. A surface like glass appears not to be homogenous when subjected to chemical agents. O. P. R. O.

Relation of H-ion concentration to flocculation of a colloidal clay (BRADFELD) 2. Mold for casting metals, glass, etc. (U. S. pat. 1,454,066) 9.

LIEBIG, B.: *Das säurebeständige Email und seine industrielle Anwendung im Apparatebau.* Ein Handbuch für die chemische Industrie, Nahrungsmittelfabrikation und andere der Chemie verwandte Industriezweige. Berlin: Julius Springer. 80 cents.

RUDOLPH, W.: *Tonwarenerzeugung.* 2nd Ed. Revised and enlarged. Leipzig: Max Jänecke. 210 pp. 4s. 3d. Reviewed in *Chemistry and Industry* 42, 379 (1923).

WARAN, H. P.: *Elements of Glass-blowing.* London: G. Bell & Sons, Ltd. 116 pp. 2s. 4d. net. Reviewed in *Chem. News* 126, 271 (1923).

**Coating glass tiles.** M. ANSPACH. U. S. 1,454,842, May 15. Glass tiles for covering walls are coated on the back with a mixt. contg. clayey earth, oil, turpentine, resinous varnish and a drier and baked at a moderate temp. The coating serves to give the back a rough surface readily adherent to mortar.

**Stacking and burning bricks.** G. E. LUCE. U. S. 1,453,850, May 1.

**Composite ceramic ware.** C. W. SAXE. U. S. 1,454,000, May 1. A portion of a ceramic article, e. g., the side walls of a filtering crucible, is formed of an impervious porcelain integrally united and vitrified with another portion, e. g., the bottom of a crucible, which is porous and is formed of Al<sub>2</sub>O<sub>3</sub> granules bonded by a vitreous clay material.

**Connected kilns.** L. WEEKS. U. S. 1,454,358, May 8. Kilns adapted for drying and burning ceramic ware are connected with each other by passages through which heated air and gases may be drawn from one kiln to another by fans.

**Refractory material from copper mat.** C. PAYTON. U. S. 1,453,993, May 1. A refractory material which is suitable for lining converters or furnaces is prepd. by blowing Cu mat without addition of SiO<sub>2</sub> and sepg. the slag formed and molding it.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

**Alumina cement.** BRICE. *Rev. universelle mines* 14, No. 2, July 15, 1922; cf. *Rev. ind. minérale* No. 44, 315(1922).—A description of a cement which is not attacked by sea-H<sub>2</sub>O nor by H<sub>2</sub>O contg. sulfates. This resistance is due, not to fusion, but to a high % of Al<sub>2</sub>O<sub>3</sub>. Its index (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>)/(MgO + CaO) is greater than 1 with a low % SiO<sub>2</sub>. C. C. DAVIS

**Plaster of Paris.** A. BRITAIN AND C. ELLIOTT. *J. Soc. Chem. Ind.* 42, 154-62T (1923).—The properties of plaster depend on the method, temp., and time of calcination. The setting time and tensile strength are influenced by the state of subdivision, both properties increasing with the degree of fineness. Gypsum accelerates setting but decreases tensile strength. Over 3% gypsum is an impurity. Slow setting anhydrite produced at moderately high temp. retards setting, while dead-burnt plaster and natural anhydrite act as inert impurities reducing tensile strength. The setting time increases and tensile strength decreases with an increase of water used in gaging. The adoption, in England, of standard methods of testing plaster of Paris is advocated. R. L. B.

LOZACH, P.: Agglomérés et pierres artificielles. Paris: *Revue des matériaux de construction et de travaux publics*. 39 pp. Reviewed in *Chimie et industrie* 9, 434 (1923).

VUGNON, M.: L'industrie des agglomérés et pierres artificielles. Paris: *Revue des matériaux de construction et de travaux publics*. 145 pp. Reviewed in *Chimie et industrie* 9, 433(1923).

**Cement.** K. G. WENNERSTROM. Can. 230,266, Apr. 10, 1923. To a molten mass of raw material such as lime, clay, sand, bauxite, ashes, etc., a mixt. of lime and sand, 20-65% by wt. of raw material, is added and the mixt. heated to form silicate. An elec. current is then passed through the material to give the cement produced good hydraulic properties.

**Hydrocarbon cement.** W. S. BARRIE and L. CHADWICK. U. S. 1,455,598, May 15. A cement adapted for luting, paving or building construction is prepd. by heating pitch or tar with a sulfate of Al, Ca or Ba.

**Magnesium cement.** SADAICHI SATO and ICHIJURO SATO. Japan. 41,180. Dec. 19, 1921. A mixt. of MgO and MgSO<sub>4</sub> is prepd. by treating powdered MgO (6 mols.) with H<sub>2</sub>SO<sub>4</sub> of 50° B<sub>e</sub>. (1 mol.). In this case 1 part of MgO is changed into MgSO<sub>4</sub> and the resulting mixt. is a dry powder. On mixing with H<sub>2</sub>O, it forms a hard mass.

**Artificial stone.** W. E. WILLETT. U. S. 1,454,780, May 8. Particles of pulverized coke are coated with fluosilicic acid, for use in artificial stone together with other ingredients such as cement and H<sub>2</sub>O.

**Recovery of potassium compounds from cement-kiln flue dust.** F. W. HUBER. U. S. 1,453,797, May 1. Flue dust from cement manuf. is treated with sufficient lime to produce a ratio of CaO:SiO<sub>2</sub> of not less than 2:1 and this material together with the carbonaceous reducing material at least about equal in amt. to the K<sub>2</sub>O present, is heated to at least 600° but below the temp. at which any large amt. of the K compds. would be volatilized. Sol. K compds. thus formed are extd.

**Rotary horizontal cement kiln.** S. S. McGRATH. U. S. 1,453,851, May 1. The kiln is slightly inclined and cylindrical for most of its length with a frustoconical flare at the discharge end to facilitate discharge from the kiln. The lining at the discharge end of the kiln is thicker than that of the main portion of the kiln.

**Building material from city refuse.** G. SCHLÖSSER. U. S. 1,454,082, May 8. See Brit. 187,066 (C. A. 17, 1121).

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

**Microscopic study of the Freeport coal bed, Pa.** REINHARDT THIESSEN and A. W. VOORHEES. Carnegie Inst. Tech. Coöperative Mining Courses, *Bull.* 2(1922).—The Freeport bed varies vertically with the lower benches rich in "anthraxylon," the proportion of which diminished towards the top of the bed, which ends in a layer of

cannel coal composed almost entirely of attritus. Variation is found with the benches. The attritus is rich in oil and tar-producing constituents. Microspore extines are characteristic of the Freeport bed.

R. L. BROWN  
**Brown coals of Victoria.** H. HERMAN. Geol. Surv. Vict., *Bull.* 45, 1922; *Australian Soc. Abstracts* 1, 9.—A description is given of the history, geography, geology, high- and low-temp. distn., coal-tar products, briquetting, boiler use, pulverizing, gas production and paleontology of brown coal. The principal areas are the Latrobe Valley, Port Albert, and Altona. Age probably Miocene to Oligocene. One or more seams aggregating several hundred feet thick, at a max. nearly 800 ft., proved over several hundred sq. mi. Chem. analyses and exptl. figures of gas yields, coal-tar products, etc., are given.

H. G.  
**Some factors in the spontaneous combustion of bituminous coals.** J. D. DAVIS AND J. F. BYRNE. Carnegie Inst. Tech. Cooperative Mining Courses, *Bull.* 3(1922).—A lab. method for detg. the relative tendency for spontaneous firing was devised and this test employed in studying the factors involved in spontaneous combustion. The rate of oxidation is proportional to the surface exposed or to the degree of fineness of the coal. Coal of less than 200 mesh had a critical temp. of 171°, while 10 to 20 mesh gave 231°. Coal dust and moisture facilitate oxidation and consequently heating. Pyrites had but small influence. Partly oxidized coal seemed to act as a deterrent to heating when mixed with fresh coal. The "anthraxylon" or "woody" constituents of the coal showed a lower critical temp. than the "attritus"; however, coals richer in "anthraxylon" did not show low critical temps. The rate of heat generation at slightly elevated temps. is very rapid compared with its dissipation by cond. of the coal. General heat dissipation by convection currents must occur to avoid dangerous temps.

R. L. BROWN  
**Available hydrogen in coal and a direct method for its estimation.** J. D. DAVIS. *Ind. Eng. Chem.* 15, 594-6(1923).—The sample (0.1 g.) is burned in an electrically heated combustion pipet, contg. a red-hot Pt spiral, in the presence of a measured vol. of O. An analysis is then made for CO<sub>2</sub> and the residual O. The vol. of O originally drawn into the pipet and that added during the combustion are measured. The amt. of O remaining after the combustion is detd. by analysis. The difference between the total O used and that consumed in the combustion of the C is equal to the vol. of O necessary to burn the available H in the coal. It is necessary to correct for the O required to burn the org. and pyritic S in the coal, and also for the expansion produced by the N. The cor. vol. of O used, multiplied by 2 gives the vol. of available H, from which the wt. can be readily calcd.

C. T. WHITE  
**The specific gravity and moisture content of coal.** T. J. DRAKELEY AND W. O. JONES. *J. Soc. Chem. Ind.* 42, 163-6T(1923).—To develop a standard method of prepn. for coal samples for sink-and-float tests 3 possibilities are considered: (a) coal samples completely satd. with water, (b) perfectly dried and (c) air dried. Under (a) cubes of coal were immersed in water; cold, boiling, and cold and boiling, each under reduced pressure. Satn. was best effected by placing coal 2 hrs. in water boiling at atm. pressure but even this was judged to be an impractical method. Under (b) samples of wet coal were placed in desiccators; over H<sub>2</sub>SO<sub>4</sub>, over CaCl<sub>2</sub> soln. of sp. gr. 1.35, and over H<sub>2</sub>SO<sub>4</sub> with pressure reduced to 2 mm. Drying took place most rapidly in the last case, but required from 15 to 20 hrs. before the coal reached a nearly const. sp. gr. so the method was considered too slow for industrial uses. As a result of the expts. on (c) D. and J. conclude that for industrial washery practice drying the samples of coal for 24 hrs. in a room of reasonably const. humidity is satisfactory for prepg. the samples for the sink-and-float detn. For more accurate work storing the samples over a salt soln. such as CaCl<sub>2</sub> of 1.35 sp. gr. is recommended. In drying coal in air some O is absorbed. The authors show that when coal is dried in streams of N or of H some of these gases are absorbed, less of the H than of the N, but always the % decrease in wt. of the sample is slightly less than the % moisture evolved. Four tables of data and 2 sets of curves summarize the results obtained in these expts.

W. W. HODGE  
**Miners' nystagmus.** J. S. HALDANE, et al. *Iron & Coal Trades Rev.* 104, 557-9 (1922).—The essential factor in the production of miners' nystagmus is deficient illumination due to the low illuminating power of the safety lamps in general use by the miners. The ordinary gaseous impurities in mine air have no direct influence on the disease. The disease is common in Belgium, France and Germany where safety lamps are almost universally used, very uncommon in America where open lights and elec. lamps are used, and very rare in Japan where acetylene lamps are generally used for lighting. Some general considerations on illumination are given.

J. L. WILEY  
**Coal miners' nystagmus: effect of the volatile constituents of coal on the incidence**

of nystagmus. FREDERICK ROBSON. *Iron Coal Trades Rev.* 106, 415-6, 456(1923); cf. Haldane, preceding abstract.—R. puts forth the hypothesis and proves it by means of statistics that coals do give rise to nystagmus in some ratio to their volatile content, the volatile content being an index of the kind of coal giving rise to the ailment. *Ibid* 598-9, 632(1923).—R. discusses further phases of nystagmus as: lamps, in relation to nystagmus; physiological aspect; CO poisoning; S, oxidation, blasting and bacterial action, and summarizes the findings of the researches. J. L. WILEY

Refractive index investigations of liquid power fuels. HANNS ECKART. *Brennstoff-Chem.* 4, 24-5(1923).—The  $n_D^{20}$  for the following org. liquids has been detd.: gasoline ( $C_4H_{10}$ - $C_8H_{18}$ ), 1.40718-1.41479; petr. ether, 1.36550-1.37641; acetone, 1.35998;  $CHCl_3$ , 1.44482;  $CCl_4$ , 1.46041;  $C_2H_5Cl$ , 1.45053;  $C_2H_5Br$ , 1.47820;  $C_2H_5I$ , 1.49509;  $C_2H_5Cl$ , 1.50348;  $C_2Cl_4$ , 1.50180; cyclohexanol, 1.46559; cyclohexanone, 1.44883;  $Et_2O$ , 1.35394;  $C_2H_5OH$  abs., 1.36192; amyl alc., 1.39963; Pr alc., 1.38613;  $C_3H_8$ , 1.50124; toluene, 1.49490; xylene, 1.49765; tetralin, 1.54678; decalin, 1.47918. C. T. WHITE

Use of alcohol as a fuel. MULLER. *Congrès Production Coloniale Marseilles* 1922, 197-201.—A discussion of the necessity of using alc. as a substitute for petroleum products, showing the success attained along this line by the use of "natalite" ( $EtOH$  54.5,  $Et_2O$  44.5, ammonia 1%). A. PAPINEAU-COUTURE

Modern British gas works. C. H. S. TUPHOLME. *Gas Age-Record* 51, 603-10 (1923).—A description of the Carlisle works with Glover-West vertical retorts and waste-heat boilers. Extensive use was made of concrete in the construction. J. L. WILEY

Functions and duties of the chemist and the bearing of chemistry on the gas industry. G. H. CHEMELL. *Gas J.* 162, 220-1(1923); *Gas World* 78, 367-9. J. L. W.

The treatment and composition of lignite tars. II. Systematic investigation of the composition of lignite tar. S. RUHMANN AND E. ROSENTHAL. *Z. angew. Chem.* 36, 153-6(1923).—Gas-producer tar from lignite and briquets was purified by the method of Frank (*C. A.* 17, 2043), vacuum-distd. up to  $260^\circ$  at 30 mm., and the distillate steam-distd. By treatment of the latter distillate successively with dil.  $H_2SO_4$ ,  $Na_2CO_3$ , and NaOH for the removal of the bases, acids and phenols, a neutral oil was obtained, the examn. of which constituted the present investigation. It was sepd. by fractional distn. at 12 mm. into 17 portions of 5" b. range, and each portion was subjected to elementary and sulfur analyses and sp. gr. detns. All fractions contained sulfur, varying from 1.89 to 3.46%. The sp. gr. fell between 0.916 and 0.926 at  $17-21^\circ$ . The freshly distd. oils had a pleasant odor. The lowest fraction, b. around  $80^\circ$ , was clear, with a light yellow color; the next fractions had a blue fluorescence; the higher fractions were opaque. They turned brown on standing, even when stoppered, but on re-distn. regained the original color. The analysis and sp. gr. of the colored oil differed little from the freshly distd. The coloring is considered due to oxidation as it is hastened by blowing with air in the presence of light and heat. The neutral oils are mixts. of pure hydrocarbons and S and O compds. The  $135-140^\circ$  fraction contained such paraffins as  $C_{16}H_{34}$  and  $C_{17}H_{36}$ . Of aromatic hydrocarbons, only traces of naphthalene and durenene were found. The sepn. and identification of the S compds., amounting to 10% of the neutral oil, proved troublesome. They were not aliphatic nor thiophenes, since treatments with metallic Na in the first case, and with  $HgOAc$  in the second, failed to remove the sulfur. Selective solvents, MeOH or  $Ac_2O$ , served partially to sep. the S compds., which were concd. in the ext. along with the unsatd. hydrocarbons and the O compds. The method of Heuser for the detection of the naphthenes (by successive treatments of the oil with dil., concd. and fuming  $H_2SO_4$ , by which the unsatd. and aromatic hydrocarbons are sepd. while the paraffins and naphthenes remain unchanged) did not give conclusive results with the higher-boiling oils, since the higher homologs of  $C_6H_6$ , such as hexaalkylbenzene, are also insol. in  $H_2SO_4$  and may be mistaken for naphthenes. The presence of naphthenes has not been established. C. B. EDWARDS

The composition of crude tar benzines. F. FRANK AND H. ARNOLD. *Z. angew. Chem.* 36, 217-8(1923).—Results are given of an investigation of crude benzines obtained from the distn. of a coal (Dinslaken, G.) at  $400-500^\circ$ . The liquid consisted of 20% aliphatic hydrocarbons and 80% aromatic and naphthalene hydrocarbons. A fractionation gave the following results: (1)  $27-60^\circ$ , 24%, sp. gr. 0.682; (2)  $60-80^\circ$ , 14%, sp. gr. 0.720; (3)  $80-120^\circ$ , 24%, sp. gr. 0.766; (4)  $120-180^\circ$ , 32%, sp. gr. 0.866; (5)  $180-220^\circ$ , 5.6%, sp. gr. 0.936. It is noteworthy that the fraction boiling at  $80-120^\circ$  contained neither  $C_6H_6$  nor toluene. C. T. WHITE

Equipment layout for washery to clean coal as prelude to making metallurgical coke. ANON. *Coal Age* 23, 781-5(1923); illus. E. J. C.

Desulfurization of coke by air. A. R. POWELL. *Bur. Mines, Repts. Investigations* No. 2469, 6 pp.(1923).—S in coke is found as  $FeS$ ,  $SO_4$ , adsorbed free S and S held in

solid soln. in the C. By air treatment it was hoped to oxidize the FeS and remove the free S formed. It was known that such a treatment would not remove the solid soln. form of S, but the removal of sulfide S would be beneficial from a metallurgical standpoint. The tests were made on coke of 2-3 in. diam. At temps. near 500° it is possible to oxidize the larger part of the FeS to Fe<sub>2</sub>O<sub>3</sub> and S, without causing appreciable oxidation of the coke itself. The free S formed from the above oxidation is retained in the coke in adsorbed form, and cannot be removed by vacuum treatment at 500°, or by increasing the temp. to 650°. Alternate repeated roasting and vacuum treatment increased the elimination of free S, but the major part remained in the coke. This investigation has indicated that the industrial desulfurization of coke by air treatment is not practical as far as the methods which have been tested would apply. C. T. WHITE

The determination and causes of the easy combustibility of coke. F. FISCHER, P. K. BRÄUER AND H. BROCHE. *Brennstoff-Chem.* 4, 33-9 (1923).—An app. is described and a method given whereby it is possible to compare the burning temp. of various cokes. This method depends upon the reduction of CO<sub>2</sub> to CO by the heated coke and a subsequent measurement of the vol. of the latter in a buret over NaOH soln. Coke (30-mesh) is heated to 300° to drive out occluded gases and placed in a porcelain tube. The air is completely driven out of the app. with CO<sub>2</sub>. The temp. is raised to 400° and increased at the rate of 50° every 10 min. A flow of CO<sub>2</sub> at the rate of 35 cc. in 10 min. is then maintained, the CO<sub>2</sub> being absorbed in a buret contg. 50% NaOH. The temp. at which the gas is not entirely absorbed is noted, and the temp. raised another 50° or 100°. This causes a marked increase in the vol. of CO, and the exact temp. at which this vol. increase takes place is considered as the burning point of the coke. Tarry residues remaining in the coke retard its burning. C. T. WHITE

Increasing ammonia yields in coke-oven practice. R. A. MORR. *Colliery Guardian* 125, 578-9 (1923); cf. C. A. 17, 1883.—Mixts. of gases with 1-2% NH<sub>3</sub> were passed over contact materials at coke-oven temps. and the amt. of NH<sub>3</sub> was detd. With "chattered" firebrick contg. much Fe<sub>2</sub>O<sub>3</sub>, decompn. began at 650° and was complete at 800° for coal gas and for H<sub>2</sub>. With coal gas contg. 3% H<sub>2</sub>O, the temp. was 50° higher for a given decompn. With N, decompn. began at 550° and was complete at 650°. Decompn. was less in dry coal gas contg. 1% O than in O-free gas. With old firebrick contg. 1.5% Fe<sub>2</sub>O<sub>3</sub> and with fused SiO<sub>2</sub>, only 10% decompn. occurred at 800° and 30% at 900°. When fused SiO<sub>2</sub> was thickly covered with C from decompn. of the gas, decompn. was only 12% at 900°. 25% H<sub>2</sub>O completely prevented dissociation of NH<sub>3</sub> at a temp. 50° higher than that for complete dissociation with dry gas. Fe<sub>2</sub>O<sub>3</sub> is undesirable in coke or bricks in any coke oven, particularly where salty coals are coked. Since dissociation of NH<sub>3</sub> is greatest when the 2 hot zones have met and all gas passes through hot coke at approx. the end of 22 hrs., steaming during the 22-6 hr. period should increase the NH<sub>3</sub> yield by preserving the NH<sub>3</sub> already formed, by increasing the nascent H according to the Tervet reaction and by increasing the gasification of N in the coke. C. C. DAVIS

Hydrolysis of starch, cellulose and peat (BUĐNIKOV, SWORYKIN) 28. Fertilizing with gas water (RÄMY, WEISKER) 15. Determination of the temperature of combustion (POLITZER) 2. Furnace for roasting ores or for destructive distillation (U. S. pat. 1,454,798) 9. Removing water from colloidal substances [peat, coal, sludge] (U. S. pat. 1,455,728) 13.

BARTEL, FRIEDRICH: *Torfwerke, Gewinnung, Veredelung und Nutzung des Brennstoffes unter besonderer Berücksichtigung der Torfkraftwerke.* Berlin: Julius Springer. \$2.20.

CHAMBERLAIN, H., COBB, J. W., LESSING, R., SINNATT, F. S., and STOPES, M. C.: *Coal. A Series of Lectures on Coal and its Utilization.* London: Colliery Guardian Co., Ltd. 41 pp. 5s. Reviewed in *Bull. Imp. Inst.* 20, 661 (1922).

LEVY, L. A.: *Gasworks Recorders: their Construction and Use.* London: Benn Bros., Ltd. 246 pp. 35s. net. Reviewed in *Nature* 111, 350 (1923); *Ind. Eng. Chem.* 15, 654 (1923).

MANVILLE, O.: *Production économique de la vapeur.* Paris: G. Donis. 1007 pp. Fr. 25. Reviewed in *Chimie et industrie* 9, 435-6 (1923); *Bull. soc. ind. Mulhouse* 88, 747 (1922).

Fuel mixture. L. ROBISON. U. S. 1,454,410, May 8. A fuel is prepd. from pulverized paper 400 lbs., finely divided coke 800 lbs., slack coal 400 lbs., soda 5 lbs., MeOH 5 gals, and coal oil 4 gals.

**Briquetting fuels.** H. A. MUELLER. U. S. 1,453,988, May 1. Saw dust, coal dust, air-dried peat or similar materials are treated with superheated steam until the air in the material is expelled and, while the mass still is filled with condensable vapors, it is compressed and the steam is condensed to bring the particles into close contact with each other.

**Dephlegmating vapors from bituminous or other materials undergoing distillation.** I. MOSCICKI. U. S. 1,455,546, May 15. Vapors produced from the distn. of coal, wood or similar substances are led upwardly through a dephlegmating column adapted to condense out a single component such as a tarry fraction and a large portion of the condensate which forms in the column is cooled slightly below its condensing temp. and forced into the upper part of the column.

**Purifying waste combustion gases.** J. C. TATE. U. S. 1,455,414, May 15. Combustion gases from hydrocarbon fuels or similar waste gases are purified and deodorized by treatment with a compn. formed of lime 14-18, charcoal 0.5-2, burned gypsum 6-10 and kaolin 2-6 parts.

**Dehydrating alcohol with kerosene.** H. E. BUC. U. S. 1,455,072, May 15. Alc. is mixed with 20-50% of kerosene, distd. with lime and the dehydrated alc. is separately condensed. Alc. thus obtained is suitable for use in *fuels* and some hydrocarbons may be condensed with it for this purpose.

**Furnace retort.** C. E. RICHARDSON. U. S. 1,454,338, May 8. A furnace retort adapted for distn. of coal is provided with a longitudinal inner wall or retort shell supported by flat bottom saddles spaced from their supports by flat sheets of Cu and asbestos.

**Water gas.** J. E. LEONARZ. Can. 230,652, May 1, 1923. A body of C is maintained over a fused bath of metal and steam is passed through the bath and C.

**Apparatus for purifying gas.** K. COX, R. P. KERR and E. J. BARTY. U. S. 1,453,754, May 1. Gas contg.  $H_2S$  is led through a contact mass such as oxides of Fe, Al and Mn in which pipes are embedded for the passage of steam, hot  $H_2O$  or other temp.-controlling medium. The latter first passes around a passage connecting the contact chamber with a S separator to which the gas is subsequently led.

**Evaporating ammonia liquor.** F. F. MARQUARD. U. S. 1,455,299, May 15. Crude  $NH_3$  liquor from by-product coke plants is passed down through a baffle tower against an upward current of hot gas. Liquor is sprayed into the path of the gas and against the lower baffles; all of the liquor is collected in the lower portion of the tower and is recirculated through the tower until the desired degree of concn. is effected.

**Coke oven.** P. GOFFART. U. S. 1,455,527, May 15.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Bibliography of petroleum and allied substances in 1919 and 1920.** E. H. BULLOUGH. U. S. Bur. of Mines, *Bull.* 216, 374 pp.(1923).—There are 4532 entries and author and subject indexes.

**Fire hazards and fire extinction.** J. S. S. BRAME. *Petroleum World* 20, 202-6 (1923).—Statistics on fire losses in the petroleum industry are given. Causes of fires and various methods used in combating fires are discussed.

**The petroleum deposits of Czechoslovakia.** K. FRIEDL. *Petroleum Z.* 19, 376-81 (1923).—The geological formations in the petroleum fields of Czechoslovakia are described. Analyses from the various fields are as follows:

Location of field.	Age.	Sp. gr.	Distg. to 200°.	Sulfur content.	Paraffin content.	Org. acid content.
Egbeil	Sarmat	0.9349	3.5%	0.25%	0.0%	1.43%
Göding	Mediterran	0.9416	3.0%	0.20%	0.0%	1.42%
Bohuslowitz	Eosän	0.7815	76%	0.026%	2.3%	...
Turzowka	Eosän	0.8399	30%	0.024%	7.9%	0.06%
Mikova	Eosän	0.7943	61%	...	3.6%	0.14%

The first two oils are young tertiary oils and the last three are "Flysch" oils. It is thought that these two types of oil have no connection and are of separate origin.

D. F. BROWN

**Properties of Egyptian petroleum.** M. A. RAKUSIN. *Petroleum Z.* 19, 412-3 (1923).—A sample of Egyptian "Mazut" showed the following analysis:  $d_{15}$  0.916,

viscosity (Engler at 50°) 4.98, paraffin content 11.7%, cold test in 15 mm. tube +18°, in 28 mm. tube +15°, flash 125° (Pensky-Martins), resin content 38% (detd. according to Rothe) and S 1.17%. Distd. under vacuum it gave

Temp.	Wt. %.	Sp. gr.	Color.
80-130	3.9	0.8498	yellow
130-170	8.2	0.8598	yellow
170-200	18.0	0.8750	yellow
200-230	15.2	0.8894	orange black
230-270	24.0	0.9061	orange black
residuum	28.8	..	black
loss	1.9		

D. F. BROWN

**Breaking petroleum emulsions.** T. KUCZYNSKI. *Petroleum Z.* 19, 420-1(1923).—The known methods of breaking emulsions are enumerated. Expts. have been carried out for breaking emulsions of Galician petroleum by the use of phenol. The amt. of com. phenol necessary to break an emulsion resistant to heat-pressure treatment is 0.1-0.3% at about 40°, and at 100° 0.01% of phenol is sufficient. The advantages of the method are saving of vapor, min. gasoline loss and the low gravity of the crude oil recovered, almost no investment as compared with other processes and the low cost of the process.

D. F. BROWN

**Crude oil emulsions of Tzientea.** K. STAUS. *Petroleum Z.* 19, 327-31(1923).—A peculiar crude oil from Tzientea, Rumania, is distinguished from other Rumanian oils by its coffee-brown, turbid color and its viscous consistency. One l. of this oil dild. with light benzine and centrifuged showed a sludge content of 40%. Three distinct layers sepd. out, the lowest one being clear water without sediment but contg. a considerable quantity of acids, especially naphthenic acids. The uppermost layer of crude oil appeared black in reflected light and had a  $d_{40}$  of 0.900, and after dild. with benzine and centrifuging showed a sediment of 0.72%, water 0.04% and an upper layer of emulsion of 2.4%. Between the uppermost layer and the water layer appeared a viscous red-brown emulsion of about  $\frac{1}{10}$  the vol. of the uppermost layer. On centrifuging this layer 0.2% sediment, 18% water and a brown emulsion layer of 22% were obtained. Various means of breaking this natural emulsion are discussed.

D. F. BROWN

**Use of the super-centrifuge in the American petroleum industry.** P. DE CHAMBRIER. *Bull. lab. pétrole* 1, 159-66(1922).—Outline of the use of the Sharples super-centrifuge in America for dehydrating crude petroleum, purification and dehydration of mineral oils, and sepn. of paraffin from crude oils.

A. PAPINEAU-COUTURE

**Pressure-temperature chart for hydrocarbon vapors.** E. R. COX. *Ind. Eng. Chem.* 15, 592-3(1923).—An arbitrary logarithmic chart is described for showing the relation between the temp. of a satd. vapor and the temp. of steam at the same pressure. The chief advantage claimed for the chart is that by it closely approx. values can be easily derived from a single b. p. where other data are not available.

D. F. BROWN

**The manufacture of lubricating oils from Mexican crudes.** H. L. KAUFFMAN. *Nat. Petroleum News* 15, No. 19, 105-10(1923).—It is possible to obtain from Mex. crude oil of 20° Bé. gravity, 10% of lubricating oil of viscosity 100 at 100° F. and 4.5% of oil of viscosity 250 at 100° F. The most efficient method consists in removing the wax from the distillates resulting from steam distn. of the crude. An exptl. run on Panuco crude oil of 12.6° Bé. with steam to asphalt of about 40-50 penetration gave 42% of light oils and 54% of asphalt with 4% loss. Rerunning the cut from 38 to 60 viscosity at 100°, representing 15% of the total distillate, gave 25% of residue which could be worked up for light spindle oils. A redistn. of the fraction from 60 viscosity at 100° to asphalt of desired, penetration representing 20% of the total distillate, showed that there could be produced both non-viscous pale oil stocks, and viscous red oil stocks in fairly large proportions. The best yields of lubricating stocks are obtained by rerunning the pressed distillate for a max. yield of high viscosity bottoms in spite of the relatively high treating and filtering losses in this method. The distillate should be treated before pressing. A summary of processing and yields in running Mex. crude oil for lubricating stocks is given.

D. F. BROWN

**The cracking of petroleum oil in the gas-liquid phase.** G. EGLOFF. *Ind. Eng. Chem.* 15, 580-3(1923); cf. C. A. 17, 2045.—The importance of cracking in gasoline manuf. is discussed. The chief disadvantage of catalytic cracking is its cost. The liquid-gas cracking processes of the Burton type are limited to certain gas-oil stocks. The chief features of the Dubbs process are described and it is claimed that a wide



range of charging stocks may be successfully used in this process. Diagrams of the app. are given.

**Modern methods of cracking oil show considerable development.** H. L. DEBAR. *Oil & Gas J.* 21, No. 52, 26, 102-4 (1923).—A brief description and comparison of the Burton, Coast, Fleming, Cross, Dubbs, Muehl, and Jenkins processes. D. F. BROWN

**Treatment of natural gas gasoline to meet the "doctor test."** D. B. DOW. *Nat. Petroleum News* 15, No. 20, 99-111 (1923); cf. *C. A.* 16, 1313.—The design and operation of a treating plant for natural gasoline are described. The gasoline rises through a tower partially filled with sodium plumbite soln. and baffled with steel shavings. It passes thence to a water scrubbing tower and thence to storage. The plumbite soln. is made up of a 20% soln. of NaOH and 7% of PbO. A small amt. of S is also added. This is preferably added in a gasoline soln., 1 gal. of satd. gasoline soln. per 100 gals. of gasoline treated usually being sufficient. The PbO should be added to cold NaOH soln. D. F. BROWN

**Distillation by the aid of natural gas.** W. FRIEDMANN. *Petroleum Z.* 19, 367-75 (1923).—Expts. are described in which natural gas and still gases are used in the place of steam for distn. of petroleum. An absorber filled with active C is placed in series after the condenser and the non-condensable hydrocarbons are thus recovered from the gases passing through the condenser. It was found that by careful manipulation emulsions contg. as much as 30% of H<sub>2</sub>O could easily be dehydrated in this way and at the same time valuable hydrocarbons contained in the natural gas recovered. Numerous tables are given of data covering expts. on various original materials. D. F. BROWN

**The composition of spirits of turpentine. Separation of the constituents and their behavior in some commercial syntheses.** GEORGES DUPONT. *Recherches et inventions* 4, 345-58, 369-79 (1923).—See *C. A.* 16, 4339-40, 4072. A. PAPINEAU-COUTURE

DALLONI, M.: La géologie du pétrole et la recherche des gisements pétrolières en Algérie. Alger: J. Carbonel. 324 pp. 48 figs. Reviewed in *Chimie et industrie* 9, 223 (1923).

**Petroleum Register.** 1923 Jan. ed. New York: Oil Trade Journal. 432 pp. \$10.00. Reviewed in *Iron Age* 111, 1124 (1923).

**Uniting gases with hydrocarbon oils.** H. B. SNYDER. U. S. 1,454,567, May 8. A highly compressed gas of the CH<sub>4</sub> series (e. g., natural gas) is treated with a hydrocarbon oil which is injected into the compressed gas and the mixt. is then treated with an elec. arc while still under compression in order to effect a chemical union between the constituents and obtain a product which contains lighter hydrocarbons than those of the oil used.

**Cracking hydrocarbon oils.** J. H. ADAMS. U. S. 1,455,376-7, May 15. Crude kerosene, gas oil or other oil to be treated is preheated to a temp. somewhat below that of vaporization and is then sprayed into a closed chamber under pressure where it is brought into contact with material heated to a cracking temp. and also into contact with superheated steam. Uncracked material is refluxed and cracked vapors are led to a condenser. Cf. *C. A.* 17, 466.

**Treating heavy hydrocarbons for pipe-line transport.** J. P. PRESCH. U. S. 1,454,485, May 8. Gas (e. g., air) is supplied through heated tubes and mixed with heavy oils to facilitate their passage through pipe lines.

**Apparatus for cracking hydrocarbons.** H. A. WIER and S. A. WIER. U. S. 1,454,142, May 8. A horizontal main still is mounted within a furnace housing and connected with a horizontal secondary still mounted above it within the same housing but having its ends projecting outside the housing. Pipes extend from the top of the main still upwardly through the bottom of the secondary still and terminate above the bottom of the latter. The secondary still is connected with a condenser.

**Purifying mineral oils.** E. E. ARNOLD. U. S. 1,454,593, May 8. A mineral oil, e. g., crude oil or a distillate, is treated with liquid anhydrous NH<sub>3</sub> in the presence of Na cyanate or other similar oxidizing compd. to cause combination between the NH<sub>3</sub> and S present to form an NH<sub>4</sub>-S-O compd. which may be removed from the oil by washing with H<sub>2</sub>O.

**Distilling petroleum.** V. T. GILCHRIST. U. S. 1,455,437, May 15. Petroleum vapors are passed through a fractionating column to a condenser, the reflux condensate is reheated and vapors from it are again led through the fractionating column and to the condenser.

**Breaking up petroleum emulsions.** E. E. AYERS, JR. U. S. 1,454,616, May 8.

Na resinate is dissolved in  $H_2O$  and free rosin or other material which will produce a soln. miscible with petroleum and the soln. thus formed is added to petroleum emulsions, e. g., crude oil and salt  $H_2O$  emulsions. U. S. 1,454,617 relates to the prevention of formation of water-in-oil emulsions by the use of Na resinate solns. in  $H_2O$ , rosin and "fuel oil" or other miscible solvent.

**Horizontal still for petroleum.** J. M. MAHONEY. U. S. 1,455,642, May 15.

**Apparatus for electric treatment of hydrocarbon vapors and gases.** J. L. McCABE. U. S. 1,455,088, May 15. The app. is adapted for connection with the dome of a still. It comprises a vertical non-conducting tube provided with electrodes and elec. heating app., for producing a motor fuel from the vapors and added H.

**Electric apparatus for dehydrating petroleum emulsions.** F. W. HARRIS. U. S. 1,455,139, May 15.

**Portable apparatus for condensing vapors from gases.** G. G. OBERFELL and G. A. BURRELL. U. S. 1,455,407, May 15. The app. is adapted for commercial recovery of gasoline from natural gas by absorption in activated charcoal and subsequent distn.

**Tanks and screens for filtering oil.** C. A. HAMILTON and B. F. NOYES. U. S. 1,454,112, May 8.

**Wax-filtering apparatus.** G. H. FIFIELD. U. S. 1,455,436, May 15. Wax is filtered out from chilled oil on a filter surface through which a heat conductor extends transversely for heating the wax thus deposited.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

**Recent investigations on the composition of wood and lignin.** WAHLBERG. *Svensk Pappers Tid.* 26, 28-9(1923).—W. discusses the results of Schmidt and Graumann and those of Willstätter and Kalb on the treatment of incrustations with  $ClO_2$  and on the decompn. products of lignin and other similar substances. W. SEGERBLOM

**International paper and pulp statistics.** K. G. HAGSTRÖM. *Svensk Pappers Tid.* 25, 420-3(1922); 26, 7-8, 62-3(1923).—Statistical tables are given showing 1922 monthly exports of all grades of pulp and paper from Sweden, Norway, Finland, Canada and other countries together with monthly production and prices of paper and pulp in the United States. W. SEGERBLOM

**Red-colored sulfite pulp.** H. E. WAHLBERG. *Svensk Pappers Tid.* 25, 401-2(1922); cf. C. A. 16, 4061.—The causes of the red color in pulp are reviewed. From investigations of 2 samples of bleached and of raw pulp W. concludes that the reddening of sulfite pulp is due to the oxidation by air of the sulfite, to the Fe salts and even to the org. compds. contained in the pulp. Wine-red ferric salts are produced. The reaction is hastened by moist air, by such oxidizers as wash water, or by traces of Cu salts. The reddening can be prevented by using digesting acid free from Fe. The red color can be destroyed by washing with water acidified with  $H_2SO_4$ . W. SEGERBLOM

**The microscope in the paper-mill.** JAMES STRACHAN. *Proc. Tech. Sec. Paper-makers Assoc. of Gt. Britain and Ireland* 3, Pt. 2, 296-303(1923).—The microscope is a valuable means of study in the identification of fibers, fillers, dirt spots and sizing materials. It may also be used for controlling the beating operation and as an aid in the production of mech. pulp. Its use can be extended in the mill, saving much time in testing. An outline of microscopic research is given, with a bibliography and a list of equipment, necessary for routine work as well as for research. F. G. RAWLING

**Rubber latex in paper making.** FREDERICK KAYE. *Proc. Tech. Sec. Paper-makers Assoc. of Gt. Britain and Ireland* 3, Pt. 2, 200-22(1923); cf. C. A. 16, 4062; 17, 341.—The addn. of rubber latex increases the tensile, bursting and tearing strengths of papers which have had the same beating treatments. A paper made of leather waste with the addn. of 4-5% of latex is several times as strong as a material compounded of waste leather and 25-30% of rubber. Asbestos packing and millboard can be made by the addn. of latex to the beater, instead of using rubber solvents. The "broke" from a paper machine using furnish contg. a small proportion of latex has not caused much trouble when run again over the machine. F. G. RAWLING

**Physics of calendering.** J. STRACHAN. *Proc. Tech. Sec. Papermakers Assoc. of Gt. Britain and Ireland* 3, Pt. 2, 223-8(1923).—Increases in pressure, time of contact, moisture and friction in the "nips" produce a smoother finish up to a certain point, after which the paper is weakened. A momentary hydration of the cellulose due to high pressure is said to account for the increased translucency to light and the alteration

in color of some dyes during calendering. Microscopic examn. and staining reactions support this theory.

FRANCIS G. RAWLING

Hydrolysis of starch, cellulose and peat (BUDNIKOV, SWORYKIN) 28. The chemical decomposition of plant fibers. Textile fiber and cellulose production (SCHWALBE) 25. Physicochemical study of nitrocellulose in organic media (KUGELMASS) 2.

DIECKMANN, RICHARD: Die Fabrikation des Zellstoffes aus Holz. I Teil. Sulfitzellstoff. Berlin: Otto Elsner Verlagsgesellschaft.

GRUNEWALD, W.: Herstellung und Verarbeitung von Druckpapieren. Berlin: Verlag Carl Hofmann. 164 pp.

Pulping paper stock. F. P. MILLER. U. S. 1,455,594, May 15. Raw paper is first treated in a digester to soften the pulp and paper and the material discharged from the digester is subjected to the action of a jet of  $H_2O$  under pressure. The pulp is then allowed to flow with the  $H_2O$  through a screen, coarse and fine stock are sep'd., strings and the like are removed from the coarse portion and the latter is again mixed with the fine portion. The combined stock is passed over a screen and fine particles passing through the screen are led to a stuff chest and coarse particles retained by the screen are led to a beating engine, reduced, screened and then also led to a stuff chest.

Coloring paper. L. P. WINCHENBAUGH and L. GENTILE. U. S. 1,454,363, May 8. Finished dry paper is colored by application of a soln. of a dye in a volatile org. solvent of low viscosity, *e. g.*, a soln. of a coal-tar dye in alc. or gasoline, so that some of the soln. penetrates the paper. Solns. of different color may be successively applied. U. S. 1,454,364 relates to a similar process.

Use of starch products in making colored lines on marbled, glazed, and calendered papers, and cardboard. RINGE & Co. Ger. 369,470, Aug. 21, 1921. The color is mixed with starch products to which is added  $FeSO_4$  in soln. The resulting paper can be written on with ink.

Bleaching paper pulp. R. B. WOLF. U. S. 1,454,610, May 8. Paper pulp is lifted to the top of a bleaching tank (through which it subsequently descends) by a conveyor within a central vertical tube which is made narrower at the bottom than at the top to prevent wedging of the descending pulp between the conveyor tube and the tank wall.

Sizing and waterproofing. CARL JAGER. Ger. 364,564, Jan. 11, 1921. Insol. naphthenates are produced in the beater.

Removal of printers' ink, etc., from paper. CHEMOTECNISCHE GESELLSCHAFT. Ger. 369,468, Mar. 22, 1921. Old paper stock is treated with hydrogenated phenols, which are converted into water-sol. substances, either alone or in combination with other solvents.

Pulp from straw or similar material. C. BACHE-WIIG. U. S. 1,455,471, May 15. Straw, corn stalks or similar material is treated with NaCl to soften it without destroying the ligneous matter and is then cooked with a bisulfite liquor to obtain pulp.

Fibers from the potato plant for the manufacture of paper. HEINRICH EGGERS and ADOLF BURLIN. Ger. 370,197, Nov. 19, 1920. The washed and comminuted potato plants are cooked under 2-3 atm. pressure in a 2% NaOH soln. After washing and disintegration, the resulting mass is bleached in a 4 to 5% chloride of lime soln. with continuous agitation. A treatment with  $NaHCO_3$  soln. completes the process.

Deodorizing cellulose pulp. G. A. RICHTER. U. S. 1,454,339, May 8. Sulfate pulp is freed from disagreeable odors by treating it with an oxidizing agent such as a small amt. of  $Ca(OCl)_2$  which will react with the odorous substances without materially altering the color of the pulp.

Cellulose aralkyl ether composition. H. DREYFUS. U. S. 1,454,960, May 15. An alkylsulfonamide, such as  $MeC_6H_4SO_2NH_2$ , is used with aralkylated cellulose derivs., *e. g.*, benzyl cellulose deriv., to produce compns. which may be used for varnishes, films, filaments or molded articles. Cf. C. A. 16, 493.

Cellulose ether composition. H. DREYFUS. U. S. 1,454,959, May 15. A compn. adapted for making films, varnish or elec. insulation is formed of ethyl cellulose ether and  $PhSO_2NHMe$  or other similar alkylsulfonamide prep. which is liquid at ordinary temp. and becomes more viscous and gelatinous when cooled to low temps., together with other usual ingredients.

Nitrocellulose compositions. H. DREYFUS. U. S. 1,454,961, May 15. Xylene monomethyl (or monoethyl) sulfonamides or similar alkyl sulfonamides are used with nitrocellulose in prep. compns. which are adapted for use in making varnishes, films or molded articles.

**Composition for setting viscose.** W. H. STOKES. U. S. 1,455,679, May 15. Starch is mixed in a finely divided condition with  $\text{H}_2\text{SO}_4$  of such diln. and temp. (preferably a concn. of about 28% and a temp. of about 28–30°) that no gelatinization occurs and there is then added, with stirring, sufficient concd.  $\text{H}_2\text{SO}_4$  to yield a homogeneous product of the desired concn. adapted for use in setting threads or filaments from viscose.

**Setting bath for viscose.** J. A. LLOYD. U. S. 1,455,630, May 15. A bath for setting viscose is formed by dissolving starch in  $\text{H}_2\text{SO}_4$  of 50–65% concn. at a temp. of about 35–75°.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

**Charles Edward Munroe.** H. W. WILEY. *Ind. Eng. Chem.* 15, 648–9(1923).—A brief biography, with portrait. E. J. C.

**Forty-seventh annual report H. M. Inspectors of Explosives.** A. COOPER-KEY. London (pamphlet) 1923, 36 pp.—For the first time on record no fatal accident has occurred during the year in a factory established under the Explosives Act and but 11 persons were injured by the 51 accidents that were reported. Among the accidents recorded is that of Knowles engaged in breaking down small arms ammunition which resulted in conviction for manslaughter; of killing of a woman mixing  $\text{KClO}_3$  and S; of 1500 tons of propellant explosives at Fort Falconara, Spezia, Italy, Sept. 28, 1922 caused by successive lightning strokes, the extensive damage to the adjacent town of S. Terenzio being due to the "recoil wave" produced by the vacuum following the explosion and to the projection of heavy debris from the Fort; and of an explosion at Brotherton's Colour Works at Bromborough June 16, 1922 from grinding a mixt. contg. picramic acid.

CHARLES E. MUNROE

**The factors determining the choice of materials for stone-dusting of mines.** A. C. DUNNINGHAM. *J. Soc. Chem. Ind.* 42, 195–200T(1923).—The British Dept. of Mines, to prevent the propagation of explosions in coal mines, requires mines to be so treated with incombustible dust that the dust on the floor, sides and roof of the mine contains not more than 50% of combustible matter. The regulations as to the nature of dust to be used are that, when the material is dried, 50% shall pass a sieve with 200 meshes per linear in. and that this dust shall not be injurious to the health of the miners. Ground shale or ground limestone have been the generally used materials. D. believes pptd.  $\text{CaCO}_3$  in colloidal condition superior. Its apparent d. is 1.17 with 1.62 and 1.68 for ground shale and ground limestone, resp. It best satisfies the requirements of stonedust that it should be (1) incombustible, (2) very finely divided, (3) have a large surface relative to mass and be amorphous and porous, (4) dry, (5) harmless to health, (6) uniform in order to simplify proper control over the stone-dusting process, (7) white or very light in color.

CHARLES W. MUNROE

**Preventing dust fires and explosions.** D. J. PRICE. *Chem. Met. Eng.* 28, 902–3 (1923).—Deals with the general principles governing such fires and explosions but emphasizes the importance of the removal of static or accumulated dust, which supplies material for secondary explosions. When explosion occurs in a plant that has been recently cleaned and when effective dust-collecting methods have been practised the explosion is localized and of minor extent.

CHARLES E. MUNROE

**Annual report, explosives division, Department of Mines of Canada for 1922.** G. OGILVIE. Ottawa, 1923, 20 pp.—Accidents in manuf. recorded are: an explosion of dynamite in cartridgeing, due probably to striking a blow on a film of dynamite in or about the hopper with an Al dust-pan; of gunpowder in a corning house, due to friction on bearing or a static charge; and of Thompsonite in mixing, due to breaking of a paddle in the mixer; the effects produced in each case are noted. Other accidents were in a detonator charging machine, due to insufficient lubricant about a post to keep any compn. falling about it moist; the firing of a S pot in a detonator factory, due to scrapings from the work bench having been added to the pot in violation of instructions; burning of a workman exposed to chlorate dust who, contrary to regulations, went to the mess-room without removing his working clothes where his coat ignited at the stove; nitro-glycerin accumulated in the waste acid tanks of a denitration system decomposed and exploded; and a fire in a dope house attributed to packing in somewhat close confinement bags of  $\text{NaNO}_3$  received from the drier are a few of many noted.

CHARLES E. MUNROE

**The effect of pressure on the limits of inflammability of mixtures of the paraffin hydrocarbons with air.** W. PAYMAN AND R. V. WHEELER. *J. Chem. Soc.* 123, 426–34

(1923).—Mason and Wheeler (*C. A.* 12, 996) found that increased initial pressure, above atm., tended to narrow the limits of inflammability of mixts. of H and of CO with air at both the upper and lower ends of the scale but that with  $\text{CH}_4$  + air mixts. while limiting at the lower end the upper limit was extended as the pressure was increased. In the present investigation, it was found that mixts. of air with other paraffin hydrocarbons behave like  $\text{CH}_4$  + air. Tests at reduced pressures gave results in good agreement with those obtained at pressures above atm.

CHARLES E. MUNROE

**The disintegration of explosives.** OTTO POPPENBERG. *Z. angew. Chem.* 36, 80-5(1923).—The compn. of the products of detonation of an explosive in a closed space, such as a bomb, after they have slowly cooled is held to be different from that obtaining at the moment when detonation has just been completed, the change being dependent on the variation, with the temp., of the equil. constns. of such reactions as are possible between the gaseous components of the products. Hence to det. quant. the true compn. of the products existing when detonation is just completed means must be provided for suddenly chilling the products to the "frozen condition." P. believes this is accomplished by firing the charge in a small bomb enclosed in an evacuated larger bomb, holding that the energy expended in bursting the small bomb and the sudden expansion of the detonation products are combined, sufficient to effect the result sought. This may also be accomplished by firing the explosive within a chamber in a double-walled bomb, the space between the walls of this being filled with water or Hg so that the detonation products may be quickly and intimately mixed with the liquid and suddenly cooled. Exptl. firings were made with picric acid, TNT and trinitrobenzene and the results showed satisfactory agreement with those calcd. from theoretical considerations, thus supporting the cooling theory advanced. Small, but material amts. of HCN are recorded in the products of each of the explosives above named.

CHARLES E. MUNROE

**The problem of dust explosions in industry.** W. E. GIBBS. *Chem. Age* (London) 8, 54-6, 92-4(1923).—Deals chiefly with factory dusts, classifying them after Wheeler as (I) dusts which ignite and propagate flame readily; the source of heat required for ignition is comparatively small, such as a match flame; (II) readily ignite but require to propagate flame a source of heat either of large size and high temp. such as an elec. arc, or of long duration such as the Bunsen flame; (III) dusts which are not capable of propagating flame because they (a) do not readily form a cloud in air, or (b) contain a large quantity of incombustible matter, or (c) the material does not burn fast enough. Sugar stands at the top of Class I. A dust-air mixt. differs from a gas-air mixt. in the degree of intimacy of contact between the components of the system regarded both statically and dynamically. The sp. surface of the dust is enormous as compared with the same substance in massive form, and under suitable conditions of concn. it can, when ignited, burn with explosive violence. 100 g. of starch dust in a cu. m. of air constitutes a very explosive mixt. Assuming the dust particles are spherical and of an av. diam. of 0.001 cm. there will be about 100,000 particles per cc. of air. These will be about 0.02 cm. apart, and the total surface area of 100 g. of dust will exceed 30 sq. m. A small proportion of finer dust particles of, say, 0.00001 cm. diam. would effectively occupy the intervening spaces and, by their ceaseless agitation, would form a connecting link between the coarser particles in much the same way a small amt. of inflammable gas would serve to communicate ignition from one particle to another. The theory is developed in minute detail and a great array of data from expts. given.

CHARLES E. MUNROE

**The development in evaluating explosives from their maximum energy during the last fifty years.** H. KAST. *Z. angew. Chem.* 36, 72-5(1923).—This is largely an historical review accompanied by a bibliography but with new matter on  $\text{NH}_4\text{ClO}_4$  and  $\text{NH}_4\text{NO}_3$ , showing that while the former salt is normal in its behavior toward initial detonating substances the behavior of the latter is erratic and the results are lower than called for by theory. In the decompn. of  $\text{NH}_4\text{NO}_3$ , side reactions occur and even with the most powerful initiator it does not detonate but only decomposes explosively. The true rate of detonation of  $\text{NH}_4\text{NO}_3$ , calcd. from that of  $\text{NH}_4\text{ClO}_4$ , is 50% greater than the latter. While nitrated hexamethylenetetramine (hexogen),  $\text{C}(\text{CH}_2\text{ONO}_2)_4$ , and mannitol hexanitrate occupy the highest places in order of effectiveness,  $\text{NH}_4\text{ClO}_4$  and  $\text{NH}_4\text{NO}_3$  occupy the lowest. A valuable table of the energy contents and efficiencies of some 12 important explosives is given.

CHARLES E. MUNROE

**Mixtures of TNT and tetryl.** M. GRUA. *Giorn. chim. ind. applicata* 5, 75(1923).—G. claims priority (1919) as against Taylor and Rinkelbach, in finding that in mixts. of TNT and tetryl there is present a mol. compd. of the 2 components.

ROBERT S. POSMONTIER

Physicochemical study of nitrocellulose in organic media (KUGELMASS) 2. Recovery of ether from gases (U. S. pat. 1,455,707) 13. Action of Phenylenediamine on  $\beta$ - and  $\gamma$ -trinitrotoluene (Giua, Giua) 10.

**Blasting explosive.** A. J. STRANE. U. S. 1,455,309, May 15. A propellant blasting powder is formed of mixed grains, some of which consist entirely of colloided nitrocellulose powder and some entirely of black blasting powder.

**Nitrocellulose powder containing nitroguanidine.** J. M. SKILLING. U. S. 1,454,414, May 8. A propellant explosive powder contg. nitrocellulose and nitroguanidine is superficially impregnated with a detergent material such as dinitrotoluene.

**Nitration apparatus.** H. V. WALKER. U. S. 1,454,870, May 15. Nitration of cotton or similar material is effected by reaction with nitration acids in a rotatable nitrating drum having an interior peripheral helical partition forming a succession of pockets for limited bodies of the mixt. U. S. 1,454,871 relates to nitration in a similar app. in which the charges of mixed cotton and acids are conveyed from the point of charging to the extn. app. in a succession of intermittent movements with gentle agitation.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

**Dyes, dyers and dyeing fifty years ago.** J. W. EASTBURN. *Am. Dyestuff Rep.* 12, 363-8(1923). E. J. C.

**Cotton Research Company's accomplishments.** E. D. WALLEN. *Textile World* 63, 749-51(1923).—A brief description of their work and the progress made. C. E. M.

**Four important cotton reds.** ANON. *Textile World* 63, 2087-9(1923).—A table is given for the identification of *p*-red, turkey red, primuline and naphthol AS.

CHAS. E. MULLIN

**Progress in cotton dye manufacture during 1922.** O. R. FLYNN. *Textile World* 63, 949-51(1923).—A brief discussion of the use of J-acid in dye manuf., and the manuf. of roseanthrene A, O and R, diazo light red 7BL, diazo bordeaux 7B, zambsi black V, benzo fast black L, solamine blue FF, fast blue 2GL and 4GL, a light fast red, fast yellow 4GL and 5GL, diamine scarlet B, Congo brown R, Congo fast blue R, erica pink and diaminocatechol.

CHAS. E. MULLIN

**Increasing brightness of colors.** J. F. SPRINGER. *Textile World* 63, 1169, 1189 (1923).—In dyeing silk with acid dyes the shade is brightened by avoiding the use of boil-off liquors,  $\text{Na}_2\text{SO}_4$ , mineral acids and high temps.

CHAS. E. MULLIN

**The development of Naphthol AS Red.** W. CHRIST. *Textilber.* 4, 230-1(1923).—In the dyeing of Naphthol AS Red, the tendency of the diazo soln. to become alk., by the introduction of NaOH absorbed by the cotton from the naphthol bath, may be checked by adding  $\text{Al}_2(\text{SO}_4)_3$ .

E. R. CLARK

**Dyeing stripe effect unions.** L. G. HAYES. *Color Trade J.* 12, 100-1(1923).—Formulas are given for dyeing white and colored silk stripe effects in unions contg. a Lustron stripe.

CHAS. E. MULLIN

**The effect of metallic hydroxides on the fastness to light of indigo dyeings on cotton.** R. HALLER. *Textilber.* 4, 229-30(1923).—Pieces of indigo-dyed cotton fabric were printed with a thickened soln. of various metallic salts, passed through NaOH soln., washed and dried. Portions of the printed and unprinted material were exposed to direct sunlight during July and August. The pptd. hydroxides of Fe, Mn, Ni, Co, Cu, and Ag increased the resistance of the dyeing to light in the order named. The hydroxides of Mg, Al, Zn, Hg, Pb, Bi, Cd, Sn, Au and Pt had no practical effect.

E. R. CLARK

**Heavy sizing practice.** E. RUEF. *Textile Am.* 39, No. 2, 33(1923).—Removal of size before dyeing, printing or finishing is unnecessary if the sizing was properly done with suitable materials.

CHAS. E. MULLIN

**Use of zinc dust in silk printing.** BARRINGTON DEPUYSTER. *Color Trade J.* 12, 133-4(1923).—Formulas are given for white and colored discharge pastes. C. E. M.

**The truth about "Arghan," or pita floja fiber.** G. A. LOWRY. *Textile World* 63, 1155-6(1923).—This fiber is the product of the *Ananas macrodontis* or pineapple species, also known as *Bromelia karatas* or *B. sylvestris*, of which there are many varieties. In Columbia other varieties are known as chivy-chivy, maya, pinuela and penguin. It has been used for centuries in the Philippines and Columbia for cloth, rope, etc. The

fibers are very strong, 2 to 2.25 in. long, elastic, very resistant to salt water, easily dyed and may be processed with flax-spinning machinery. It grows wild in abundance and yields about 2% of fiber.

**Buying raw silk on specification.** W. P. SKEW. *Textile World* 63, 1301-3(1923).—For general classification purposes physical qualities should be based on av. of strength and cohesion tests but for a specific fabric only the test of the dominating influence need be used, with the modification that the tests omitted shall not be under a named value.

**The action of chemical and physical influences on wool and the testing of cloth for wear resistance.** SIGM. V. KAFF. *Textilber.* 4, 237-40(1923).—The wear resistance tester previously described (*C. A.* 17, 2054) was evaluated by tests of exptl. fabrics made with a lot of new wool and varying percentages of shoddy. The results in each trial showed inferior wear resistance for the adulterated fabrics, and K. considers that the device is thereby proven to be a satisfactory imitation of actual wear. Fabrics made of tightly twisted yarns wore better on this machine than those made from loose yarn. Fabric dyed with afterchrome colors showed much less wear resistance than when dyed with vat colors. AcOH in dyeing operations on wool affects the wearing quality less than HCOOH or H<sub>2</sub>SO<sub>4</sub>.

**Measurement of wool as a basis for grading.** H. B. GORDON. *Textile World* 63, 1707-13(1923).—The measurements are best made by means of a microscope with an ocular micrometer, upon fibers mounted in a mixt. of 2 vols. glycerol with 1 vol. EtOH. The suggested av. diam. in microns for fibers of various grades is: fine 20,  $\frac{1}{4}$  blood 23.5,  $\frac{1}{2}$  blood 29,  $\frac{3}{4}$  blood 33, and low  $\frac{1}{4}$  blood 35 microns.

**Structure of the cell membrane of flax and hemp.** W. MÜLLER. *Forschungs-Institut Sorau. Faserforschung* 3, 166-72(1923).—A critical review of microscopical methods for the identification of flax and hemp, with a bibliographical appendix. Evidence based on the direction of coiling of the fibers when wetted is inconclusive, since it is not based on known differences in cell structure.

**Damaging of flax by microorganisms.** G. RUSCHMANN. *Faserforschung* 3, 131-61(1923).—During retting flax may become impregnated with a variety of microorganisms; methods for the isolation of several of these are given. Damp flax fiber was seriously weakened by the development of some of these forms in a series of expts. Spore-forming bacteria as well as fungus growths aid in the tendering.

**Humidity in jute, hemp and flax mills.** A. W. THOMPSON. *Textile World* 63, 1167-8(1923).—A relative humidity of 60-65% at 24° is used for almost all the operations from carding to weaving.

**The chemical decomposition of plant fibers. Textile fiber and cellulose production.** C. G. SCHWALBE. *Z. angew. Chem.* 36, 173-6, 179-83(1923).—The chief constituents to be removed from fibers in order to obtain a pure cellulose consist of pentosans, hexosans, lignin, and wax. Pentosans and hexosans may be best brought into soln. through hydrolysis by the action of a mineral acid. Lignin is dissolved by treatment of the fiber with 5% NaOH soln. under 5 atm. pressure and at 110-25°, also by the use of CaHSO<sub>4</sub> soln. under similar conditions, or by the action of Cl. The customary treatment given cotton, retted flax, and jute to free the fibers from non-cellulose constituents consists in boiling under pressure with 5-8% NaOH soln. for 2-3 hrs. The boiling is followed by a hypochlorite bleach. A discussion is given which includes the various processes used for the treatment of pine, fir, and aspen in order to sep. the cellulose from the non-cellulose material. The method which is widely used consists in boiling the material with a CaHSO<sub>4</sub> soln. at 135-50° under 3-5 atm. pressure for 0.5-2.0 hrs.

**The identification of cuprammonia artificial silk.** KONRAD LANG. *Textilber.* 4, 231-2(1923).—Minute quantities of Cu may be detected by its catalytic effect on the reduction of ferric salts by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. (Cf. Hahn and Leimbach, cf. *C. A.* 17, 701.) Cuprammonia silk always contains enough Cu to give this test. The silk to be tested is treated with 15 cc. concd. HNO<sub>3</sub> and after 30 min. the liquid is dild. with 200 cc. H<sub>2</sub>O. Of this 50 cc. are pipetted off, 25 cc. of FeCl<sub>3</sub> soln. (32.4 g. per l.) and 2 cc. NH<sub>4</sub>SCN soln. (76.1 g. per l.) are added, and the whole is dild. to 400 cc. To this, 15 cc. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> soln. (75 g. per l.) are added and the time is noted for destruction of the color. The ext. from cuprammonia silk will be decolorized in half the time needed for decolorization of the ext. from viscose silk. Checks are run against known samples.

**Hydralin, a new dry-cleaning fluid.** R. HUETER. *Deut. Farber Ztg.* 59, 311-2(1923).—Hydralin, methylcyclohexane, is recommended as a suitable solvent for use by dry cleaners. It is non-poisonous and free from high-boiling materials.

E. R. CLARK

**Advances in our knowledge of the biological retting of fiber stalks.** FR. TOBLER. *Z. angew. Chem.* 36, 240-2(1923); cf. *C. A.* 16, 1873. E. J. C.

The combination between organic dyes and inorganic substrates (RHEINBOLDY, WEDEKIND) 2. The testing of bleach liquor (GEGENHEIMER) 7.

**Acridine dyes.** H. GRÜNHAGEN. U. S. 1,455,486, May 15. Di-formyl-*m*-tolylene-diamine and the hydrochloride of 4-amino-2-dimethylaminotoluene or similar compds. are heated together to produce a dye giving orange red tints on leather.

**Acridine dyes.** H. GRÜNHAGEN. U. S. 1,455,487, May 15. 4-Formylamino-2-methylaminotoluene and 4-amino-2-ethylaminotoluene-HCl or similar compds. are heated together to produce a dye giving a clear yellow color on leather.

**Acridine dyes.** H. GRÜNHAGEN. U. S. 1,455,488, May 15. Formyl-*m*-tolylene-diamine is heated with  $\beta$ -naphthylamine-HCl in equimol. proportions at a temp. of about 170-190° in order to form a dye coloring leather clear yellow tints.

**Sulfur dye.** E. KRAMER and L. ZEH. U. S. 1,449,681, Mar. 27. Various indophenols (e. g., that obtainable from methylbenzylaniline and quinonechloroimide) when heated in alc. with Na polysulfide produce dark blue dyes dyeing cotton greenish blue shades fast to Cl, boiling and light. In general, indophenols of the formula  $R'CH_2RNC_6H_4N:R''O$  (in which R is alkyl, R' a mononuclear arylene and R' an aryl radical) may be used as starting materials.

**Yarn-dyeing apparatus.** J. H. GILES and D. M. GILES. U. S. 1,455,247, May 15.

**Apparatus for vertical and horizontal movement of materials in dye vats.** F. P. LARIVEL. U. S. 1,454,897, May 15.

**Treating vegetable fibers.** H. C. FUELLER. U. S. 1,454,581, May 8. Spanish moss or a fibrous material of similar character is freed from plant juices by treatment with acid and alk. baths, then dyed and treated with stiffening and glossing substances, e. g., glue and  $CH_2O$ , for use in mattresses or the like.

**Cellulose acetate composition for treating fabrics.** A. MEUSELLA. U. S. 1,453,764, May 1. A liquid mixt. adapted for coating collars or cuffs is prepd. from acetone 100, cellulose triacetate 6, triphenyl phosphate or other plasticizing agent 3, castor oil 0.25-0.50, zinc white and lithopone 3 and  $BaSO_4$  0.5 part.

**Waterproofing and fireproofing fibrous materials.** A. ARENT. Can. 230,237, Apr. 10, 1923. A mixt. of a drying oil, amyl acetate and a fire-retardant Sb compd. is used.

**Waterproof cloth.** UICHIRO NAGANO and GENSHIRO MIZUSHIMA. Japan. 41,213, Dec. 20, 1921. Cloth woven from fibers previously treated with a mixt. of 20-40% water-glass soap, 30-60% sol. starch, and 10% gelatin is immersed in 10%  $MgSO_4$  soln., dried, painted with a mixt. of 25% boiled oil, 20% solid paraffin, 50% gasoline, and a small quantity of Turkey red oil, and finally rolled through hot rolls.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Zinc oxide.** E. O. RASSER. *Chem.-Ztg.* 47, 227-8(1923).—A comparison of various zinc-oxide pigments, contg. 3-6% Pb, is given with special reference to the brand "Segoldus" as manufactured by the German Govt. plant at Oker in the Harz. This latter pigment consists of about 90-92% pure  $ZnO$  and 6% Pb, and is free from such fillers as  $BaSO_4$ , chalk, or gypsum. In the burning process, the  $ZnO$  and  $PbO$  presumably undergo mol. combination, yielding a product of considerable opacity, permanence, and resistance to weathering and actinic light. Ground in oil, "Segoldus" pigment yields a hard but elastic, and glossy surface. It is more grayish than zinc white or lithopone, possesses a high degree of fineness, and is economical because of its light weight. It is an excellent substitute for other white pigments, both for interior and exterior work where a pure white is not essential. Expts. are being made on permanence of the pigment when applied to various surfaces such as stone, wood, iron, and cement.

T. F. BUEHRER

**The determination of titanic oxide in pigments with suggestions for the analysis of mixed pigments.** L. E. BARTON. *Paint, Oil and Chem. Rev.* 75, No. 9, 10-1(1923).—A pigment known as *titanox* is now on the market and has stimulated interest in the detn. of Ti pigments. A method for detg.  $BaSO_4$  and  $TiO_2$  in *titanox* is given and directions for the analysis of mixed pigments. *Analysis of titanox.* Treat 0.5 g. with 20 cc. concd.



$\text{H}_2\text{SO}_4$  and 7.5 g. of  $\text{Na}_2\text{SO}_4$ . Evap. to fumes and continue heating till all the pigment is decomposed. Cool, dil. with 100 cc. of water, filter and weigh the insol.  $\text{BaSO}_4$ , correcting for  $\text{SiO}_2$  if necessary. Run the filtrate while hot through a Jones reductor into a flask filled with  $\text{CO}_2$  and titrate the soln. with standard  $\text{Fe}$  alum soln., using KCNS as indicator. If desired, the  $\text{Ti}$  may be detd. gravimetrically by the method of Gooch. Also in *Oil, Paint and Drug Rep.* 103, No. 9, 94(1923).

**The lithopone problem.** J. FRÉRE. *Rev. prod. chim.* 26, 253-6(1923).—Brief discussion of the lack of sunlight fastness of lithopone. (Cf. Maass and Kempf, *C. A.* 17, 344; Eibner, *C. A.* 17, 1337; Roches, *C. A.* 16, 3217.) W. T. H. A. PAPINEAU-COUTURE

MITCHELL, C. AINSWORTH. *Ink*. London: Sir Isaac Pitman & Sons, Ltd. 128 pp. 3s. net. Reviewed in *Chem. News* 126, 271(1923).

**Anti-rust paint.** PAUL PETERS. *Can.* 230,310, Apr. 10, 1923. The compn. contains  $\text{Pb}_2\text{O}$  and a binder adapted to reduce the oxide during drying. Cf. *C. A.* 17, 1156.

**Oil compositions for industrial use.** H. V. DUNHAM. U. S. 1,449,976, Mar. 27. Linseed oil, rapeseed oil or other oils, emulsified and homogenized with casein and alkali or soap or with gelatin (with or without the addition of a drier, carnauba wax, dyes, lanolin, paraffin, Turkey red oil or other auxiliary ingredients), is dried to form a product which may be mixed with  $\text{H}_2\text{O}$  for coating leather or other fabrics or for making cold-water paints. The dry product may be formed with about twice as much oil as casein.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

**Olein.** H. STADLINGER. *Z. deut. Oel-Fell-Ind.* 43, 129-31, 147-9(1923).—A strong plea is made that the term "olein" be defined and its use restricted to products possessing fixed properties, which are discussed in detail from the standpoint of the consumer and the chemist. P. ESCHER

**Studies on hardening of oil. I.** The effect of some compounds upon the nickel catalyzer. GEN-ITSU KITA AND TETSURO MAZUME. *Rikugaku Kenkyujo Iho* 2, 1-8(1923).—K. and M. have studied the effect of some compds. upon the activity of metallic Ni at  $170^\circ$ , soy-bean oil (I no. 130) being used as the material. The quantities of the compds. mixed with Ni were about 2-16% of the Ni and the time of reaction was 1.5 hrs. As the addn. substances,  $\text{Al}(\text{OH})_3$ , Ca and Mg phosphates,  $\text{MgO}$ , Ca borate, stearic acid (I no. 7.3), palmitic acid (I no. 2.0), and  $\text{Na}_2\text{CO}_3$  were selected. On adding these substances to Ni they were merely mixed, (2) after mixing with NiO, the mixt. was reduced and (3) a mixt. of  $\text{Ni}(\text{OH})_2$  and the addn. substances were reduced. The results are given in tables. The effects of the addn. substances upon the catalyzer differ according to the conditions of mixing. Generally (2) and (3) gave an accelerating effect, but there was optimum quantities, which were also controlled by many conditions.  $\text{H}_2\text{O}$  having poisonous action upon weak catalyzers gives no special preventive action upon an effective catalyzer like Ni. The last 2 facts coincide with those in the case of enzyme action. K. KASHIMA

**Malabar sardine oil.** J. J. SUDBOROUGH, H. E. WATSON AND P. K. KURUP. *J. Indian Inst. Sci.* 6, Pt. II, 19-40(1923).—The constns. of 1st-grade oil are: acid value 2.7%, sapon. no. 194.0, I no. 172, insol. bromide 33.0, titer  $33.4^\circ$ , neutralization no. of fatty acids 195, mean mol. wt. of fatty acids 287. Second-quality oil with acid values up to 12 can be refined by alkalis with a loss of 8 to 10%. The oil can be hydrolyzed by castor-bean lipase, and also hydrogenated. The fatty acids are not readily hardened, owing to the rapid deterioration of the catalyst; a Ni borate-kieselguhr catalyst lasts about 12 hrs. The oil can be sulfonated; the product is semi-solid and dark-colored. E. SCHERUBEL

**Mohua oil.** J. J. SUDBOROUGH, H. E. WATSON AND D. V. CHANDORKAR. *J. Indian Inst. Sci.* 6, Pt. I, 1-17(1923).—Crude Mohua oils with acid values below 13 give a loss of 18% by alkali refining. The refined oil can be made water-white and odorless, with vegetable charcoal and with superheated steam under diminished pressure. The oil is readily hydrolyzed with lipase preps. It can be hydrogenated; and the curve obtained by plotting  $n$  against the I nos. of the hardened samples indicates that the compn. of the oil resembles that of cottonseed. The hardening of the free fatty acids from Mohua oil is difficult owing to the formation of Ni soaps and the destruction of the

activity of the catalyst. A ghee substitute is obtained by mixing deodorized oil hardened to a suitable consistency with 20% of high-grade natural ghee. E. SCHERUBEL

**Minyak nyatok** (oil from Palaquim species). C. D. V. GEORGI. *Malayan Agr. J.* 11, 38(1923).—The following consts. were detd.:  $d_{20}^4$  0.8571,  $n_D^{42}$ ,  $n_{40}$  1.4570, sapon. no. 190.6, I no. 46.6, unsapon. 0.4%, acidity 1.1%, titer 55.5°, I no. of fatty acids 40.0. E. SCHERUBEL

**Kapayang oil**. C. D. V. GEORGI. *Malayan Agr. J.* 11, 39-40(1923).—Two samples were examd., *Hodgsonia heterochita* and *Pangium edule*. The seeds of the former contd. 57.4% oil and those of the latter 21.9%. The consts. of the former were:  $d_{20}^4$  0.922,  $n_{40}$  1.4604, sapon. no. 203.9, I no. 63.6, mean mol. wt. of fatty acids 272.7, titer 40.8°, I no. of fatty acids 61.9; consts. of the latter: sapon no. 199.5, I no. 107.3. At present these oils have no economic value. E. SCHERUBEL

**Cod-liver oil industry in Newfoundland**. S. S. ZILVA AND J. C. DRUMMOND. *J. Soc. Chem. Ind.* 42, 185-8T(1923).—Newfoundland cod-liver oil is prepd. from cod livers entirely and is of high and uniform vitamin potency. The manuf. of the oil is under the control of the Ministry of Marine and Fisheries. The direct steam process is used almost exclusively; it is found to have no deleterious effect on the vitamin content of the oils. The refining processes consist in removing the stearin by chilling and straining. The stearin is used for soap making. E. SCHERUBEL

**Note on the sulfuric-acid test for liver oils**. ARTHUR HARDEN AND ROBERT ROBISON. *Biochem. J.* 17, 115-6(1923).—The purple color obtained with liver oils when agitated with  $CS_2$  or  $CHCl_3$ , to which a drop of concd.  $H_2SO_4$  has been added, seems to involve cholesterol, and perhaps fufuraldehyde. The purple color can be simulated by adding a drop of concd.  $H_2SO_4$  to a light petroleum soln. contg. both cholesterol and fufuraldehyde. This can be used as a test for a soln. contg. cholesterol. BENJAMIN HARROW

**Modern theories of detergent action**. T. H. BARRY. *Chem. Age* (London) 8, 446-8(1923).—A review. WM. STERICKER

**Cheap soaps and economy in washing compounds**. O. SPANGENBERG. *Z. deut. Oel-Fett-Ind.* 43, 257-8(1923).—S. describes the manuf. of semi-boiled soaps from fatty acids of palm-kernel or coconut oil, mixed with light-colored rosin. P. ESCHER

**The catalytic hydrogen liberation**. E. C. KAYSER. *Chem. Umschau* 30, 73-4(1923).—K. refers to W. Normann's observation of an increase in the I no. at certain stages of oil hardening (cf. C. A. 17, 1344) and points out that the presence of double C bonds would attract any nascent H and prevent its escape from the oil, thus leaving the observed increase in the I no. without any proper explanation. P. ESCHER

**Examination of formaldehyde-soap solutions**. H. KREIS AND P. WERMUTH. *Schweiz. Apoth. Ztg.* 61, 145-6(1923).—Dil. 20 g. soap soln. with about 120 cc.  $H_2O$ , and add with shaking, 25 cc. of  $CaCl_2$  soln. (5% anhydrous), dil. to 200 cc., filter. In 20 cc. of the filtrate det.  $HCHO$  by the I method of Pharm. Helv. Or, sep. the  $HCHO$  from  $H_2SO_4$  soln. by simple distn. Both methods give accurate results. Com. samples varied from 1.81 to 2.235%  $HCHO$ . S. WALDBOTT

**Ennobling or improving soaps**. E. KRÄCHTER. *Seifensieder Ztg.* 50, 97-8(1923).—A short compilation of recent improvements in the manuf. of soaps, including the use of hardened oils, the addn. of hexalin and tetralin, etc., to improve cleansing power, the addn. of ricinolic acid, casein and sapalbin to improve lathering power and general appearance and the manuf. of solid potash soap by means of  $AcOK$ . P. ESCHER

**Comparative results with carbon disulfide and trichloroethylene in sanga extraction**. O. MICHAELIS. *Seifensieder Ztg.* 50, 124-5, 139(1923).—Sanga is the residue left after pressing oil from olives. A comparison is made between the results obtained by extg. sanga with  $CS_2$  and  $C_2HCl_3$ , from a tech. and financial view-point, giving yields and prices. The results are in favor of  $C_2HCl_3$  through a better yield of oil with lower acid content, less loss by foots, less bleaching earth and smaller loss of oil retained by the latter. P. ESCHER

**Processes in the manufacture of toilet soaps**. J. LEIMDÖRFER. *Seifensieder Ztg.* 50, 123-4(1923).—A brief resumé of the principles involved in the various steps in the manuf. of toilet soaps by the customary process is followed by a short account of its manuf. by drying the boiled soap on drying rolls, mixing the resulting chipped or powd. soap in closed containers and pressing the cakes in powerful hydraulic presses, all operations being automatic; the limitations of the process and the properties which the soap base must possess for a perfect product are pointed out. P. ESCHER

Tanks and screens for filtering oil (U. S. pat. 1,454,113) 22.

LEWKOWITSCH, J.: *Chemical Technology and Analysis of Oils, Fats and Waxes*. Vol. III. 6th Ed. Revised by George H. Warburton. London: Macmillan & Co., Ltd., St. Martin's St., W. 1. 508 pp. 36s. Reviewed in *Chem. News* 126, 222(1923); *Nature* 111, 595(1923).

**Preserving cottonseed.** F. C. ATKINSON. U. S. 1,455,016, May 15. Cottonseed is preserved against fermentation by mixing with 5-10% of a dry pulverized cereal product such as starch, which may be sepd. by sieving after 10-20 hrs.

**Oil extraction.** F. P. CROFT. U. S. 1,454,705, May 8. Oil-bearing material, e. g., coconut meat, is coarsely ground, heated to dry it, ground more finely and then subjected to high pressure to express the oil.

**Apparatus for continuous extraction of oils from fruits by action of solvents.** M. WILBUSCHEWITSCH. U. S. 1,454,419, May 8. The app. is arranged to operate on the counter-current principle and solvent is recovered by distn.

**Toilet soap.** F. C. ATKINSON. U. S. 1,455,015, May 15. Toilet soap stock is mixed with corn meal 25-30% and finely ground corn-cob cellulose.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

**Progress of the past campaign (in Bohemia).** MACAS. *Z. Zuckerind. czechoslovak. Rep.* 47, 332-4(1923).—Beets averaged 18% sugar and 90% purity. Draft was 108%. Battery temps. were held below 68°. In many cases total CaO addition was held below 1.6%. In general the operation was very smooth and satisfactory in all factories.

W. L. BADGER

**Composition of juices in the past campaign (in Bohemia).** J. VONDRAK. *Z. Zuckerind. czechoslovak. Rep.* 47, 335-7(1923).—All juices showed a relatively high purity. Samples were sent by a number of factories to the central lab. of the Bohemian Association and av. compn. was as follows: (a) diffusion juice, (b) thick juice; sugar (a) 17.21, (b) 60.29; purity (a) 91.4, (b) 95.2. Calcd. to 100 sugar: ash (a) 2.66, (b) 2.06; total N (a) 0.461, (b) 0.304; albumin N (a) 0.086, (b) 0.003; amino N (a) 0.052, (b) 0.009; betaine N (a) 0.106, (b) 0.103; harmful N (a) 0.323, (b) 0.292. The abnormally high purity of the juice resulted in high-purity molasses (64-71) but the volume of molasses was smaller than usual, consequently the total sugar loss was not abnormal.

W. L. BADGER

**Practical hints about the production of high-grade sugar of good quality.** CH. A. BENJAMINS. *Arch. Suikerind.* 31, 199-201(1923).—During the past season complaints were received on account of black specks and yellow lumps in high-grade Java sugars. The former usually consist of rust or other foreign material from the pan. They can be avoided by boiling the first strikes of the campaign from sirup alone, of 20-4° Baumé, maintaining good circulation. The sugar which has picked up all the foreign particles is remelted in water or juice, filtered, and returned to the sirup supply tanks. Yellow lumps in the sugar are generally caused by insufficient steaming of the pan, leaks in the steam pipe at the centrifugal, or else they were present in the molasses used for mixing. It is best to pass such molasses through a screen before use. To get sugar crystals of good color, grain should be formed from pure sirup, and no molasses should be drawn in until the crystals are large enough.

F. W. ZERBAN

**Sugar losses in slaking lime with press wash water.** JIRI VONDRAK. *Z. Zuckerind. czechoslovak. Rep.* 47, 311-6, 319-24(1923); *Listy Cukrovar.* 41, 125(1923).—Press water was collected in a clean tank and analyzed. It was then used for slaking lime and the milk of lime was measured, sampled, and analyzed. No definite evidence could be obtained of any decompn. of sugar or decrease in purity. Sol. Ca salts were not increased. When treated in another factory in the same manner there seemed to be a loss of between 2% and 3% of the total sugar contained in the press wash water. Lab. expts. were carried out by slaking lime with sugar solns. under varying conditions. Very small amts. of sugar seemed to be decompd. An extensive study of methods of analysis showed that none of the usual methods for analyzing lime cake would recover all the sugar. If the cake was completely dissolved in dil. AcOH practically all of the sugar could be recovered. When this method of analysis was used it was shown that in no case was there an appreciable amt. of sugar lost except when insufficient H<sub>2</sub>O was used so that excessive temps. resulted.

W. L. BADGER

**Experiments with Norit.** JAR. DEDEK. *Z. Zuckerind. czechoslovak. Rep.* 47,

343-7(1923).—A first (refinery) sirup of 64° Bx., 0.005 alkalinity, was used and 1% of Norit (on wt. of actual sugar) added in the form of cakes of 40% H<sub>2</sub>O from a previous filtration. The mixt. was heated and pumped directly through presses. 240 sq. ft. filter surface took care of 100 tons sugar per day. The sirup was then passed through a 2nd filter partly filled with Norit. Pressure for filtration was 30-40 lbs. First filters ran 2-3 hrs. and then were filled, but were not running cloudy. Second filters ran 6 to 7 days. 290 gals. of hot H<sub>2</sub>O washed the cake down to 0.2 sugar. A batch of Norit was used 3 times on first products before regeneration. In 18 days operation regenerating with NaOH, 3700 tons 1st sugar were produced with 1750 lbs. of Norit, and the total Norit lost was 0.006% of the raw sugar. Av. color removal was 56%. First sirups only were clarified in this test. In a 2nd test of 13 days 3 products were clarified and the Norit was regenerated in a kiln. 9200 tons of raw sugar were refined; Norit in process was 8600 lbs., loss of Norit 0.04% on raw sugar. Color removal was 62% for 1st sirups and 33% for 2nd. In another refinery the products from Norit filters were then filtered through boneblack, resulting in a 50% increase in capacity. In another refinery, with 0.44% Norit to 100 sugar in a sirup whose color was 10° St. with fresh Norit the color removal was 46%; once-used Norit, 30%; and twice-used Norit, 12%. Compared to Carboraffin, Norit has a less decolorizing power, is coarser and hence filters better, can be used on denser sirups, is more easily regenerated, is in general easier to use, and gives a clear white product. Carboraffin often gives a product of faintly greenish tint. Presses on Norit run clear from the start; on Carboraffin they often run cloudy for 15-30 min.

W. L. BADGER

**An improved sugar refractometer.** H. C. PRINSEN-GEERLIGS. *Indische Mercuur: Arch. Suikerind.* 31, 203-4(1923).—The telescope is in a horizontal position, and the double prism is placed within reach on top instead of underneath; this makes the instrument easy to operate. The scale, in % sugar and in  $n_D$ , is read through the same telescope with which the observation is made. The sugar scale intervals are 0.2% up to 50%, and 0.1% from there to 97.5%. Instead of the cross hairs there is a small circle with a point in the center. There is also a compensator for use when other liquids but sugar solns. are to be read. Direct or reflected light can be used by simply turning the mirror. The app. is manufd. by Zeiss.

F. W. ZERBAN

**The "Halfa" apparatus for removing spent chips from diffusers.** HAMPL. *Z. Zuckerind. czechoslovak. Rep.* 47, 338-41(1923).—A discussion of types of nozzles for flushing out diffusers.

W. L. BADGER

**Directions for carrying out comparable field experiments with sugar beet seed.** JOSEF URBAN. *Z. Zuckerind. czechoslovak. Rep.* 47, 299-310(1923); *Listy Cukrovar.* 41, 235(1923).

W. L. BADGER

**Beet pests and beet diseases in 1921.** FR. RAMBOUSEK. *Z. Zuckerind. czechoslovak. Rep.* 47, 324-9(1923); *Listy Cukrovar.* 41, 87(1923).

W. L. BADGER

**An investigation of the hydrolysis of starch, cellulose and peat with hydrochloric acid.** P. P. BUDNIKOV AND A. I. SWORYKIN. *Z. angew. Chem.* 35, 677(1922).—HCl is removed from hydrolyzed solns. electrolytically rather than by neutralization. The additional advantage of the recovery of Cl is emphasized.

T. SWANN HARDING

#### Evaporation by compression (GENSECKE) 13.

**Treating molasses.** A. WOHL. U. S. 1,449,134, Mar. 20. Molasses is treated (e. g., for use in yeast propagation) with an inorg. acid and a phosphate (e. g., superphosphate and H<sub>2</sub>SO<sub>4</sub> in the proportion of 2% as much H<sub>2</sub>SO<sub>4</sub> as molasses). The acid and superphosphate may be heated together to increase the amount of P available to the yeast if the treated molasses is used for yeast production. The molasses may be heated moderately with the added substances and the ppt. which forms sepd. CaSO<sub>4</sub> may be added to effect partial removal of excess K salts.

**Decolorizing sugar solution.** SHINKICHI YAMAZAKI. Japan. 41,186, Dec. 19, 1921. Sugar soln. is agitated with about 1% Ca(OH)<sub>2</sub> and the excess of lime is pptd. with CO<sub>2</sub> or ZnSO<sub>4</sub>. The filtrate is slightly acidified with oxalic acid, warmed slightly, filtered and reduced with Zn (4 g. Zn for 600 g. of sugar) and oxalic acid at 50-70°.

## 29—LEATHER AND GLUE

ALLEN ROGERS

**Synthetic tannins.** R. B. CROAD. *J. Soc. Chem. Ind.* **42**, 203-7T(1923).—Discussion of the manuf., properties and uses of syntans prepd. in 6 different ways: (1) action of aldehyde upon hydroxysulfonic acids; (2) aldehyde upon sulfonated hydrocarbons; (3) aldehyde upon hydroxy-aromatic compd., using an acid condensing agent and subsequent sulfonation of the dry resin; (4) formaldehyde and Na bisulfite upon an aromatic hydroxy compd.; (5) formation of sulfones by the action of heat upon sulfonated hydrocarbons; (6) sulfonation of coumarone resins and heavy tar oils. Properly prepd. syntans, at concns. ordinarily used, exert no measurable hydrolytic action on unhaird calf skin. Syntans are good bleaching agents for leather and valuable in shortening the time of vegetable tanning when used in conjunction with ordinary vegetable tanning materials.

J. A. WILSON

Acridine dyes [for leather] (U. S. pat. 1,455,486-8) **25**.

WILSON, JOHN ARTHUR: **The Chemistry of Leather Manufacture.** Am. Chem. Soc. Monograph Series. New York: Chemical Catalog Co., Inc. 350 pp. \$5.00.

**Plumping leather.** J. L. ROBINSON. Can. 230,859, May 8, 1923. After chrome-tanning, leather is treated at 60° F. with a soln. of 15 parts HCHO in 100 parts water.

**Finishing dry-cleaned leather.** V. O. OLSEN. U. S. 1,453,723, May 1. A paste, for use in finishing dry-cleaned leather after addition of gasoline, naphtha or other solvent, is formed of petrolatum 30, cottonseed oil 15, and ZnO 50 parts.

**Tanning.** P. J. C. MARGOTTEN. U. S. 1,453,800, May 1. Unhaird skins are treated with a chromic acid tanning soln., treated with SO<sub>2</sub> in a closed vessel to convert the chromic acid into Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, treated with ammoniacal vapors to force out the SO<sub>2</sub>, washed with H<sub>2</sub>O to remove NH<sub>3</sub>, freed from excess H<sub>2</sub>O, subjected to alc. vapors, submerged in oil and freed from alc. by evapn. leaving oil in the skin to be oxidized by the action of the Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to exert a fresh tanning action, and finally dried. Cf. C. A. **17**, 225.

**Tanning hides.** V. PERADOTTO. U. S. 1,455,655, May 15. Mechanical features of circulation of tanning soln.

